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(54) Title: NANOSTRUCTURES FORMED THROUGH CYCLOHEXADIENE POLYMERIZATION

(57) Abstract: A nanostructure formation process that includes the step of polymerizing a diene under conditions suitable to yield a structure having at least one dimension ranging from 1 to 100 nanometers. More specifically, the self-assembly of block copolymers of styrene and 1,3-cyclohexadiene is exploited to form a cylinder-in-cylinder morphology, followed by crosslinking of poly(cyclohexadiene) (PCHD) and removal of the polystyrene (PS) segments, as a means for producing novel functionalized PCHD nanotubes. PCHD may be aromatized to poly(phenylene) (PP), a strong, crystalline, and thermally stable engineering polymer. These materials characterized in terms of their sizes, shapes, surface chemistry and mechanical properties. Composites incorporating these nanotubes can be used in a new class of robust, lightweight, high strength materials.

NANOSTRUCTURES FORMED THROUGH CYCLOHEXADIENE POLYMERIZATION

Background

Field of the Invention

5   The present invention relates to the formation of nanostructures through polymerization reactions and, more particularly, to the formation of nanotubes through the controlled polymerization of cyclohexane.

Reference to Related Art

Synthesis of PCHD

10   Synthetic polymers are an indispensable and remarkably versatile class of materials. The suitability of a polymer for a particular application is controlled by its specific structural and molecular properties such as molecular weight (MW), molecular weight distribution (MWD), local and global architecture, and functionality. To understand the relationship between

15   polymer structure and properties, there is great interest in well-defined polymers made by living addition polymerization processes. Tremendous progress has been achieved in living polymerizations over the past two decades, thanks to the development of new polymerization methodologies. Nevertheless, living anionic polymerization is still the most versatile technique

20   for synthesizing polymers with well-defined structures. Many new materials with controlled architectures, functionalities, and narrow MWD have been made using anionic polymerization. However, most of the studies are limited to several well-behaved, mostly hydrocarbon, monomers (such as styrene, 1,3-butadiene, isoprene, etc.).

25   1,3-Cyclohexadiene (1,3-CHD) polymers (PCHD) are of interest from both scientific and practical standpoints. These polymers offer the opportunity to combine microstructural control during diene polymerization with post-polymerization chemistry in order to tailor the properties of the resulting polymers. PCHD and its derivatives should have higher mechanical strength

30   and better thermal and chemical stability compared to common, i.e., vinyl, polymers due to the alicyclic structures (six-membered rings) in the main

chain. PCHD can be modified by various dehydrogenation procedures, such as bromination followed by dehydrobromination, aromatization by p-chloranil, or catalytic dehydrogenation. The C=C bond in PCHD can also be hydrogenated by either diimide or using $Pd/BaSO_4$ under H_2 pressure. It has been reported that hydrogenated PCHD has the highest Tg (231°C) of all hydrocarbon polymers. Hydrogenated PCHD polymers have good heat, weather, impact, abrasion, and chemical resistances, low water absorption, and birefringence; they also serve as good optical materials due to their excellent transparency and rigidity. The copolymer of 1,3-CHD with cyclopentadiene has been used as an active element in photomicrolithographic devices, and the optical resolution is greatly enhanced by the addition of PCHD blocks. It has also been proposed that PCHD may be useful as a plastic material for undersea applications because of its high hydrolytic stability.

There have been many reports on the synthesis of PCHD polymers. Essentially all conventional polymerization procedures have been applied to the polymerization of 1,3-CHD. These include cationic, radical, Ziegler-Natta, transition-metal complexes, and anionic polymerizations. Only low molecular weight or insoluble materials were obtained in most cases due to various side reactions. The anionic mechanism has proven to be the best way to polymerize 1,3-CHD with high conversion and molecular weight control, although side reactions, such as chain transfer and termination, have limited the maximum attainable molecular weight of PCHD. In general, the observed molecular weights are independent of conversion and do not depend on monomer or initiator concentrations under anionic polymerization conditions. The formation of benzene, cyclohexene, and 1,4-cyclohexadiene (1,4-CHD) has been observed during polymerization. Using difunctional alkali naphthalenides as initiators, molecular weights as high as 19 kg/mol (Li +) and 38.7 kg/mol (Na +) were obtained in 1,2-dimethoxyethane (DME), in which the polymer precipitates. Very recently, Natori and co-workers reported that polymerization of 1,3-CHD anionically could be controlled using certain additives. See Natori, I. *Macromolecules* 1997, *30*, 3696; Natori, I.; Inoue, S.

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Macromolecules 1998, *31*, 982; Natori, I.; Inoue, S. *Macromolecules* 1998, *31* 4687.   They   used   the   *n*-BuLi/N,N,N',N'-tetra-methylethylenediamine (TMEDA) initiation system and carried out the reaction under nitrogen atmosphere (pressure up to ~ 4 kg/cm^2) at 40°C. According to their findings, the ratio of *n*-BuLi to TMEDA and the method of introducing the chemicals are crucial for obtaining "well-controlled" PCHD (polydispersity indices < 1.1). A family of PCHD homopolymers and their copolymers with styrene, butadiene, and isoprene has been made using this method. However, all the samples with narrow MWD were less than 15 kg/mol in molecular weight. Surprisingly, other additives, even if structurally very similar to TMEDA, were found to be less effective.

Block Co-Polymers

Block copolymers, composed of thermodynamically incompatible blocks covalently bonded together, can self-assemble into well-ordered nano-domains because of the mutual repulsions between unlike chain segments and the constraints imposed by the connectivity of the blocks.   In the strong segregation limit, even the simplest linear AB diblock copolymers consisting of two flexible chains can exhibit a rich variety of morphologies depending on their volume fractions. However, it is highly desirable to be able to control the microphase morphology and the composition separately in actual applications. Consequently, this dependence of morphology on composition limits flexibility in designing new materials for specific usage. For example, if a certain purpose requires a material with a cylindrical morphology in which the component comprising cylindrical domains makes up over 50 vol % of the material, traditional neat block copolymers would not be useful.   In this composition range only lamellar equilibrium morphologies will form for typical diblock copolymers.

Two approaches have been used to uncouple this strict dependence of block copolymer morphology on volume fraction.   One approach is to introduce architectural asymmetry into the block copolymer (i.e., change the connectivity of the different blocks).   Nonlinear architectures, such as

miktoarm stars and grafted block copolymers, have been demonstrated both theoretically and experimentally to allow control of morphology independent of the familiar composition windows found in linear AB diblock morphologies. For instance, PI (PI = polyisoprene) in a 3-miktoarm star of $(PI)_2PS$ (PS = polystyrene) with about 0.81 volume fraction of PS formed randomly oriented wormlike micelles dispersed in a continuous PS matrix. Moreover, this morphology was demonstrated to be the equilibrium state of the system. This unusual morphology is presumably due to the graft architecture of the molecule and the relationship between the particular volume fraction and the concavity of the PS/PI interface on which the two PI chains per molecule must reside. At the same volume fraction and molecular weight, a linear PS-PI diblock would have PI spheres distributed in PS matrix. Also, for a regularly spaced, tetrafunctional multigrafted block copolymer (PI backbone with double PS grafts) with ~ 9 vol % PS, instead of producing PS sphere/PS cylindrical structure as predicted by Milner's theory, an unusual new morphology was formed. The morphology can be described as a microphase-separated mesh of PS struts or wormlike domains in a PI matrix. These results clearly demonstrate the effectiveness of varying molecular architecture in "decoupling" the dependence between composition and morphology for block copolymers.

The alternate approach of introducing conformational asymmetry into the diblock copolymer has also attracted considerable interest recently. In a sense, common block copolymers can be best considered as flexible-semiflexible block copolymers due to conformational asymmetry reflecting differences in the statistical segment length (chain stiffness) of the blocks. Conformational asymmetry can shift the volume fraction range over which various morphologies are observed because of different space filling characteristics of the two blocks. AB diblock copolymers consisting of a flexible coil and a rigid rod block (so-called rod-coil block copolymers) represent the extreme case of conformational asymmetry. These materials have stimulated much research interest over the past decade, and a variety of

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supramolecular architectures have been observed for rod-coil block copolymer systems. The aggregation behavior of rod-coil systems reflects two different ordering phenomena: (i) the microphase separation of the coil and rod blocks into ordered periodic structures and (ii) the tendency of the rodlike block to

5   form anisotropic, ordered structures. Even though many fantastic structures have been observed, the phase behavior, and hence the properties, of rod-coil systems are difficult to tailor because of the complexities of the interactions in the system. However, if the stiffness of one block varies systematically while keeping the other block constant, the phase behavior could be tuned in a

10   controlled manner. Lai et al. studied the phase separation of styrene-isoprene diblock copolymers and their hydrogenated derivatives (styrene-ethylene-*alt*-propylene and vinyl-cyclohexanes-ethylene-*alt*-propylene copolymers). See Lai, C.; Russel, W. B.; Register, R. A.; Marchand, G. R.; Adamson, D. H. *Macromolecules* 2000, *33*, 3461. They found that the phase behavior did

15   evolve as the conformational asymmetry parameter, ε, was varied, but not in a simple fashion. Gido, Mays, and their co-workers studied phase separation in polyisoprene-block-poly(*tert*-butyl methacrylate) (PI-PtBMA) diblock copolymers. For samples with volume fraction (Φ) > 0.30 of the "stiff" block, PtBMA, small phase boundary shifts were found, consistent with theoretical

20   predications. See Pochan, D. J.; Gido, S. P.; Zhou, J.; Mays, J. W.; Whitmore, M.; Ryan, A. J. *J. Polym. Sci., Polym. Phys.* 1997, *35*, 2629 and references cited therein. However, discrepancies were observed in the volume fraction dependence of experimentally determined morphological behavior Φ_{PtBMA} spherical micelles with weak lattice ordering in a PI matrix) and the

25   theoretically calculated morphology (cylinder) when $\Phi_{PtBMA} < 0.30$.

Recently, there was observed an unusual core-shell cylinder-in-cylinder microphase-separated morphology for the polystyrene-block-poly(1,3-cyclohexadiene) (PS-PCHD) system, which may reflect their conformational asymmetry. This asymmetry might be expected given the fact that PCHD has

30   para-linked cyclohexene rings incorporated into the main chain of the polymer.

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1,3-CHD polymers are a very interesting class of materials because of their unique structures and expected advantageous properties. Zhong and Francois synthesized PS-PCHD block copolymers using *sec*-butyllithium (*sec*-BuLi) in a nonpolar solvent by first polymerizing styrene, followed by addition of 1,3-CHD to the living PS anions. See Zhong, X. F.; Francois, B. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 411; Francois, B.; Zhong, X. F. *Makromol. Chem.* **1990**, *191*, 2743; Francois, B.; Izzilllo, S.; Iratcabal, P. *Synth. Met.* **1999**, *102*, 1211. During polymerization of 1,3-CHD, they found that chain transfer to monomer was unavoidable and that some of the metalated monomer reinitiated polymerization. They eventually converted the PCHD block to poly(p-phenylene) (PPP). Zhou also synthesized a series of PS-PCHD block copolymers using *sec*-BuLi. See Zhou, J. Ph.D. Thesis, The University of Alabama at Birmingham, 1996. He used benzene/hexane mixtures as the solvent (v/v = 9/1) and ran the polymerizations at low temperatures (<5°C) in order to minimize side reactions. Even so, chain transfer and termination reactions limited the PCHD composition in the final products. Recently, Natori and co-workers reported that anionic polymerization of 1,3-CHD could be controlled using the *n*-BuLi/N,N,N',N'-tetramethylethylenediamine (TMEDA) initiator system. See Natori, I. *Macromolecules* **1997**, *30*, 3696; Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 982. Various block copolymers of 1,3-CHD with styrene, butadiene, and isoprene were made by sequential addition of the monomers. According to their findings, living PCHD (PCHDLi) and PS (PSLi) species have similar reactivity toward styrene, whereas PSLi chains hardly react with 1,3-CHD.

Star Polymers

Constituting the simplest form of branching, star polymers are ideal for investigation into the structure-property relationships of branched polymers. The first star polymers were synthesized in 1948 through condensation chemistry. Since then, virtually all polymerization methods have been used to make various star polymers; however, all of these methods are variations of two more general methodologies. The first method involves the

polymerization of a monomer "*out of*" a multifunctional initiator. This can be an experimentally expedient and clean approach, but common practical difficulties with this method involve synthesis of an appropriate initiator and adequately promoting its efficiency. (To obtain narrow molecular weight distribution materials, all initiating sites must react quickly.) The second general method for making stars involves linking prepolymerized living polymer chains "*into*" a coupling reagent. This is by far the more extensively studied procedure. This latter approach provides the opportunity to sample and thus characterize the "arm" material before forming the star polymer and often allows mixed arm incorporation. Divinylbenzene (DVB) and chlorosilanes are the most popular linking agents used. Chlorosilanes have become the classic linking agents for the synthesis of star polymers using anionic polymerization because of the clean and quantitative nature of the linking reaction (assuming steric effects are adequately considered). On the other hand, DVB provides robust but relatively less well-defined branched materials, since precise control over the number of arms is not possible and stars produced by this method are always mixtures of materials having different numbers of arms.

Compared to the number of publications on the synthesis and properties of star homopolymers, the number of studies published on star-block copolymers, which have block copolymer arms, is quite small. Price et al. synthesized three- and four-armed star-block copolymers of styrene and isoprene (with styrene as the outer block) using chlorosilanes as linking agents. See Price, C.; Watson, A. G.; Chow, M. T. *Polymer* 1972, *13*, 333. The styrene volume fractions of their samples were fixed at about 0.24. Even though about 25% excess of living arms was used, significant amounts of three-arm (for $SiCl_4$) and two-arm (for CH_3SiCl_3) species were formed. Bi and Fetters synthesized six- and nine-armed DVB-linked polystyrene-polyisoprene stars containing ~ 25 vol % polystyrene. See Bi, L. K.; Fetters, L. J. *Macromolecules* 1975, *8*, 90. This was achieved by adding a predetermined amount of DVB compounds to a solution of living diblock chains. Later, a variety of star-block copolymers with different kind of blocks have been

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synthesized with this method. Extending their work, Bi and Fetters synthesized and studied two series of chlorosilane and DVB linked styrene-butadiene and styrene-isoprene star-block copolymers containing up to 29 arms and having approximately 27-40 vol % polystyrene (outer block). See Bi, L. K.; Fetters, L. J. *Macromolecules* **1976**, *9*, 732. They found that the synthesis of four-armed star-block copolymers was facilitated by adding several units of butadiene to the polyisoprenyllithium chain ends prior to the addition of tetrachlorosilane. The linking of the diblock chains by DVB proceeded to virtual completion in benzene without a polar promoter or end-capping. Thomas, Fetters, and co-workers studied a family of polystyrene-polyisoprene star-block copolymers (having up to 18 arms) made from the reaction of living diblock arms with chlorosilane linking agents. See Thomas, E. L.; Alward, D. B.; Kinning, D. J.; Martin, C. D.; Handlin, D. L., Jr.; Fetters, L. J. *Macromolecules* **1986**, *19*, 2197. A new equilibrium microdomain morphology, thought to be ordered bicontinuous double-diamond (OBDD), was found in certain cases. Even though the nature of the morphology was subsequently reevaluated, the salient morphological features of star-block copolymers had been clearly demonstrated by this group. Inverse star-block copolymers, $(AB)_2Si(BA)_2$, with A = polystyrene and B = polyisoprene, were prepared by the chlorosilane method using $SiCl_4$. In these materials, two arms were connected to the central silicon by their PS ends, and the other two arms were connected via their PI ends. The linking agent $SiCl_4$ was titrated with living (PI-b-PS) Li solution until two arms were linked to $SiCl_4$, as determined by size exclusion chromatography (SEC). The difunctional macromolecular linking agent was then treated with a small excess of the living (PS-b-PI)Li solution to prepare the inverse star-block copolymer. The order of the addition was dictated by steric factors. Tsiang synthesized several four-armed stars with three polybutadiene arms and one polystyrene-block-polybutadiene arm, (PS-b-PB)Si(PB)$_3$. See Tsiang, R. C. C. *Macromolecules* **1994**, *27*, 4399. The key step for this method is the successful synthesis of the pure $(PB)_3SiCl$ intermediate, which is obviously demanding. Molenberg and co-workers 18

synthesized four-armed polybutadiene-b-poly(diethylsiloxane) (PB-b-PDES) star-block copolymers by the reaction of living PB-b-PDES chains with 1,4-dimethyl-1,1,4,4-tetrachloro-1,2-disily-ethane. See Molenberg, A.; Moller, M.; Soden, W. *Acta Polym.* 1998, *49*, 45. The star-block copolymers were cross-linked by hydrosilylation of the PB double bonds with chloro-dimethylsilane followed by condensation of the chloro-silane groups with water. The resulting rubbers showed elastomeric behavior in tension and stress induced mesophase formation. All of the studies of star-block copolymer noted above focused on well-behaved monomers, mostly styrene, butadiene, and isoprene.

1,3-Cyclohexadiene (1,3-CHD)-based polymers are a structurally interesting class of material. With six-member alicyclic units in the main chain, a dramatic improvement of stabilities (thermal, chemical) and strength is expected in PCHD-based polymers. Through subsequent post-polymerization chemistry, such as aromatization or hydrogenation, PCHD can be converted to other novel materials. Marvel and Hartzell polymerized 1,3-CHD using a Ziegler-Natta catalyst system and subsequently aromatized the polymer in 1959. See Marvel, C. S.; Hartzell, G. E. *J. Am. Chem. Soc.* 1959, *81*, 448. Since then, essentially all the conventional polymerization methods have been used to polymerize 1,3-CHD. However, the best molecular weight and conversions obtained were via anionic polymerization in hydrocarbon solvent. Copolymerization of 1,3-CHD with other monomers (styrene, isoprene, or butadiene) under various anionic conditions has also been investigated. Kara et al. very recently presented preliminary results of the synthesis of PCHD stars having up to 19 arms. To produce these materials, they synthesized PCHD anions using *n*-BuLi/N,N,N'N'-tetramethylethylenediamine (TMEDA) and linked them using DVB.

Nanostructures

There has been intense interest in nanostructured materials over the past few years, with much of the focus directed towards electronic applications, for example, nanolithography. Nanotubes derived from carbon and "tubules" derived from phospholipids have also received a great deal of attention. The

former system is of fundamental interest as a true macromolecular system with a known architecture. Indeed, carbon nanotubes may be viewed as pure carbon fibers where the structure is entirely known to the atomic level, making them ideal materials for testing predictions of theoretical modeling. There is also

5   much interest in the practical properties of carbon nanotubes, due to their unique combination of dimension, structure, and topology. Key properties include: a large surface area that could be useful in mechanical and chemical applications, remarkable electronic properties (semiconducting or metallic), outstanding mechanical properties, and excellent thermal conductivity. Efforts

10   are underway to commercially exploit some of these properties. For example, the first single-molecule field-effect transistor has been built based on a single semi-conducting carbon nanotube. Self-assembly of carbon nanotubes into integrated assemblies could make nanotube electronics a practical reality. In terms of mechanical properties, elastic moduli of about 1000 GPa have been

15   measured for carbon nanotubes. There have been attempts to exploit carbon nanotubes as fillers in polymer composites, with some success, although lack of miscibility of the nanotubes with the matrix resin is a problem.

Lipid tubules are hollow phospholipid bilayer cylinders that are morphologically similar to a soda straw. They have lengths of tens or hundreds

20   of microns and diameters between 0.1 and 1 mm, making them very large relative to carbon nanotubes, which are several micrometers in length and 1-25 nm in diameter (larger sizes are for multi-walled species). To make lipid tubules useful in advanced materials applications, they may be metallized by coating with Ni or other metals; this imparts mechanical robustness and

25   conductivity to the tubules. These tubules may be used as "nano-vials" for controlled release of marine antifouling agents (release over many years) and controlled release of drugs (release over days to months). The metal clad structures also have interesting electromagnetic properties and are under investigation as miniaturized microwave circuits and as absorptive filters.

30   In addition to carbon and phospholipid nanotubes, there have been recent reports of nanotubes from metal oxides, amino acids, and organic

precursors. Despite the exciting scientific potential of these various types of nanotubes, they have serious practical limitations. For example, they are extremely expensive: purified single-walled carbon nanotubes cost about $2,000 per gram and the cost of lipid tubules is comparable. Also, it is difficult

5   to manufacture and purify the large amounts of these materials necessary for applications, although progress in scaling up single-walled carbon nanotubes is being made. Furthermore, there are limitations to the sizes that can be created, it is difficult to form ordered arrays, and the surface chemistries (important for functionalization and modifying surface interactions) are not readily

10   manipulated.

Block copolymers through self-assembly in bulk or in solution can form various nanostructures such as spheres, cylinders, vesicles, etc. Even nanotube formation has been reported for block copolymer systems by Eisenberg, although these tubes were not crosslinked and thus their stability is dependent

15   on their solvent environment. K. Yu and A. Eisenberg, "Bilayer Morphologies of Self-Assembled Crew cut Aggregates of Amphiphilic PS-b-PEO Diblock Copolymers in Solution" *Macromolecules, 31,* 3509 (1998). Liu recently reviewed work in the area of nanostructures from "functional block copolymers", where a block is crosslinkable thus allowing the nanostructure to

20   be stabilized. Liu and his co-workers have synthesized various stabilized nanostructures including star polymers, nanospheres, tadpole molecules, crosslinked polymer brushes, and nanofibers. See G. Liu, "Nanostructures of Functional Block Copolymers", *Curr. Opinion Coll. Interface Sci., 3,* 200 (1998); J. Tao, S. Stewart, G. Liu, M. Yang, "Star and Cylinder Micelles of

25   Polystyrene-block-poly(2-cinnamoylethyl methacrylate)", *Macromolecules, 30,* 2738-2745 (1997); A. Guo, G. Liu, J. Tao, "Star Polymers and Nanospheres from Crosslinkable Diblock Copolymers", *Macromolecules, 29,* 487-2499 (1996); F. Hanselwood and G. Liu, "Water-soluble Nanospheres of Poly(2-cinnamoylethyl methacrylate)-block-poly(acrylic acid)", *Macromolecules, 30,* 488-493 (1997); J. Tao and G. Liu, "Polystyrene-block-

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15   G. Liu, X. Xu, K. Skupinska, N. Hu, H. Yao, "Crosslinked Polymer Brushes Formation and Properties of Poly(isobutyl vinyloxy)ethyl cinnamate Brushes", *J. Appl. Polym. Sci.*, *53*, 1699-1707 (1994); G. Liu, L. Ciao, A. GtlO, "Diblock Copolymer Nanofibers", *Macromolecules*, *30*, 5508- 5510 (1996). Recently, Stewart and Liu reported the first synthesis of crosslinked nanotubes derived

20   from block copolymers. See S. Stewart, G. Liu, "Block Copolymer Nanotubes", Angew. Chem. Int. Ed., J2, 340 (2000). They prepared cylindrical nanocylinders of a poly(*tert*-butylacrylate-b-2-cinnamoylethyl methacrylate-b-isoprene) (PtBA-PCEMA-PI) triblock copolymer in methanol, followed by crosslinking of the PCEMA and removal of the inner PI block by ozonolysis.

25   Although this work represents a major advance, the synthesis of polymer nanotubes that have promise in opto-electronic applications and are strong and robust enough for structural applications (nanocomposites) and use as nanoprobes has not been reported.

With these nanotechnology applications in mind, the present invention

30   concerns the synthesis and characterization of a new type of nanotube based on self-assembled block copolymers of polystyrene (PS) and

poly(cyclohexadiene) (PCHD). PCHD is a structurally interesting polymer because it may be converted to poly(phenylene) (PP), a crystalline and chemically and thermally stable material, by aromatization. Furthermore, doping of PP will generate a conducting synthetic metal. Poly(phenylene) nanostructures have recently been reviewed. It is believed that PP "can adopt a pivotal role in synthesis-driven approaches toward molecular electronics since they combine the advantage of extended pi-conjugation with their ability to self-assemble into various supramolecular patterns." For example, ordering of PP chains into lamellar superstructures would lead to novel light emitting diodes. Use of PCHD as a precursor to PP will also avoid the major difficulty associated with synthesizing or processing high molecular weight poly(phenylene): it is an insoluble and intractable material. On the other hand, PCHD of high MW (> 30,000 g/mol) is soluble in some common organic solvents.

Summary of the Invention

The anionic polymerization of 1,3-cyclohexadiene (1,3-CHD) using various initiating systems and with or without additives is disclosed. In contrast to the situation with linear conjugated dienes, common anionic initiators in the absence of additives fail to produce poly(1,3-cyclohexadiene) (PCHD) with controlled molecular weight (MW) and narrow molecular weight distribution (MWD) because of side reactions. However, certain additives change the nature of the polymerization dramatically. Monodentate additives do not yield controlled polymerization, while some polydentate additives, such as N,N,N',N'-tetramethylethylenediamine (TMEDA), 1,2-dimethoxyethane (DME), and 1,4-diazabicyclo[2.2.2]-octane (DABCO), are effective in minimizing side reactions, if combined with the suitable butyllithium isomer. For example, the synthesis of PCHD samples with narrow MWD and good MW control is possible using the *n*-BuLi/DME/0°C or *sec*-BuLi/DABCO/20°C in benzene. The "living" character of these polymerizations is disclosed.

Additionally, the synthesis of block copolymers of 1,3-cyclohexadiene (1,3-CHD) and styrene under various conditions is disclosed. *sec*-Butyllithium

alone can initiate the polymerization of 1,3-CHD but does not yield a living process due to chain transfer and termination reactions. However, certain additives such as tetramethylethylenediamine, dimethoxyethane, and 1,4-diazabicyclo[2.2.2]octane, combined with the suitable butyllithium isomer, can be used to improve control of the polymerization of 1,3-CHD. Using these initiator systems, well-defined poly(styrene-block-1,3-cyclohexadiene)s with a wide range of compositions were synthesized and thoroughly characterized. In addition, the rate of crossover reactions during block copolymer formation and the "random" copolymerization of 1,3-CHD and styrene is disclosed.

The synthesis of well-defined, near-monodisperse, three-arm star and star-block copolymers based on poly(1,3-cyclohexadiene) (PCHD) is also disclosed. The stars were prepared by the reaction of living anionic chain ends of PCHD, poly(styrene-1,3-cyclohexadiene) (PS-PCHD), and poly(1,3-cyclohexadiene-styrene) (PCHD-PS) with CH_3SiCl_3 in benzene. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was used to control the anionic polymerization of 1,3-CHD; it also acted as a promoter during the linking reaction. The star polymers were fractionated to remove excess arm material and thoroughly characterized by size exclusion chromatography, matrix-assisted laser desorption ionization time-of-flight mass spectrometry, and light scattering.

Finally, the self-assembly of block copolymers of styrene and 1,3-cyclohexadiene is exploited to form a cylinder-in-cylinder morphology, followed by crosslinking of poly(cyclohexadiene) (PCHD) and removal of the polystyrene (PS) segments, as a means for producing novel functionalized PCHD nanotubes. PCHD may be aromatized to poly(phenylene) (PP), a strong, crystalline, and thermally stable engineering polymer. These materials characterized in terms of their sizes, shapes, surface chemistry and mechanical properties. Composites incorporating these nanotubes can be used in a new class of robust, lightweight, high strength materials. By controlling molecular weight and processing conditions, nanotubes of varying radius, wall thickness, and aspect ratio can be obtained. By varying the composition of the block

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copolymer, other shapes besides tubes (cylinders, plates) can also be made. Reactive hydroxyl groups present on the surface of these molecular objects can be used to manipulate their processing characteristics and to provide strong bonding to matrix materials. The PP nanotubes may be insulating or they may be made conducting by doping. Such materials could also be used as a component in a smart composite designed to transmit an electronic signal if, for example, impacted by a projectile. Opto-electronic and nanoprobe applications are also envisioned for these materials.

Brief Description of the Drawings

Reference is made to the accompanying drawings, to wit:

Figure A. Possible Reactions of PCHD Anion with 1,3-CHD.

Figure B. Block copolymers prepared by polymerization of 1,3-CHD with *sec*-BuLi in benzene followed by the addition of styrene (A); Styrene polymerized by *sec*-BuLi in benzene followed by addition of 1,3-CHD without use of any additive, the PSLi initiated the polymerization of 1,3-CHD (B).

Figure C. The synthesis of star polymers.

Figure D. The synthesis of star polymers

Figure E. Synthesis of diblock copolymer of PS and PCHD with ester bond.

Figure 1. SEC traces of PCHD from sec-BuLi in benzene at 0°C: (a) polymerization time 2 h; conversion ~ 43%; (b) polymerization time 6 h, conversion ~ 51%.

Figure 2. SEC traces of PCHD from (a) n-BuLi/DME at 0°C, Mn = 11.3 kg/mol, Mw/Mn = 1.07; (b) sec-BuLi/DABCO at 20°C, Mn = 13.8 kg/mol, Mw/Mn = 1.03.

Figure 3. SEC traces of PCHD from n-BuLi/DME at 0°C: (a) aliquot from first dose of monomer, Mn = 18.4 kg/mol, Mw/Mn = 1.08; (b) aliquot from second dose of monomer, Mn = 19.7 kg/mol, Mw/Mn = 1.68.

Figure 4. SEC traces (eluent THF) of PS-PCHD from sec-BuLi in benzene (styrene polymerized first). (A) Monomer charge: styrene/1,3-CHD) 93/7 (mole); (a) Mn = 14 100 g/mol, Mw/Mn = 1.06. (B) Monomer charge:

styrene/1,3-CHD = 53/47 (mole); (b) PS block, Mn = 15 100 g/mol, Mw/Mn = 1.04; (c) PS-PCHD block before fractionation, Mn = 22 400 g/mol, Mw/Mn = 1.22; (d) fractionated solution Mn = 16 400 g/mol, Mw/Mn = 1.07; (d) fractionated solid, Mn = 28 200 g/mol, Mw/Mn = 1.05.

Figure 5. ^{1}H NMR spectra of PS-PCHD SEC from sec-BuLi in benzene (a) before fractionation, PCHD wt %) 38.4; (b) after fractionation (solid), PCHD wt %) 43.1; and (c) after fractionation (solution), PCHD wt %) 12.9.

Figure 6. SEC traces (eluent THF) of PCHD-PS from sec-BuLi in benzene (1,3-CHD polymerized first). (A) Monomer charge: styrene/1,3-CHD) 35.2/64.8 (mole); (a) PCHD block, Mn = 5800 g/mol, Mw/Mn = 1.07; (b) PCHD-PS diblock, Mn = 10 100 g/mol, Mw/Mn = 1.09. (B) Monomer charge: styrene/1,3-CHD = 38.6/61.4 (mole); (c) PCHD block, Mn = 8100 g/mol, Mw/Mn = 1.13; (d) PCHD-PS block, Mn = 13 300 g/mol, Mw/Mn = 1.28. g/mol, Mw/Mn = 1.07; (b) third sampling, Mn = 13 200 g/mol, Mw/Mn = 1.11; (c) final product (6 h), Mn = 14 200 g/mol, Mw/Mn = 1.14.

Figure 7. Compositions of PCHD in PS-PCHD copolymer (from the polymerization of 1,3-CHD and styrene simultaneously using sec-BuLi in benzene) vs polymerization time.

Figure 8. SEC traces (eluent THF) of PS-PCHD from the polymerization of 1,3-CHD and styrene simultaneously using sec-BuLi in benzene: (a) first sampling, (20 min), Mn = 5600 g/mol, Mw/Mn = 1.07; (b) third sampling, Mn = 13 200 g/mol, Mw/Mn = 1.11; (c) final product (6 h), Mn = 14 200 g/mol, Mw/Mn = 1.14.

Figure 9. MALDI-TOF-MS spectra of PS-PCHD polymers: (A) "random" copolymer, Mn = 5900 g/mol, Mw/Mn = 1.03; (B) diblock copolymer, Mn = 15 400 g/mol, Mw/Mn = 1.01.

Figure 10. SEC traces (eluent THF) of PS-PCHD from n-BuLi/TMEDA/cyclohexane/40°C: (a) styrene polymerized first, Mn = 23 700 g/mol, Mw/Mn = 1.09; (b) 1,3-CHD polymerized first.

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Figure 11. SEC traces (eluent THF) of PS-PCHD from sec-BuLi/DABCO/benzene: (A) styrene polymerized first: (a) PS block $Mn = 8300$ g/mol, Mw/Mn = 1.07; (b) PS-PCHD diblock before fractionation, $Mn = 15$ 100 g/mol, Mw/Mn = 1.05; (c) PS-PCHD after fractionation, $Mn = 15$ 300 g/mol, Mw/Mn = 1.03. (B) 1,3-CHD polymerized first: (d) PCHD block, $Mn = 15$ 700 g/mol, Mw/Mn = 1.09; (e) PS-PCHD diblock before fractionation, Mn = 43 200 g/mol, Mw/Mn = 1.10; (f) PS-PCHD diblock after fractionation, Mn = 44 300 g/mol, Mw/Mn = 1.08.

Figure 12. ^{1}H NMR spectra of PS-PCHD SEC from sec-BuLi/DABCO/benzene: (A) 1,3-CHD polymerized first, fractionation solution, PCHD wt % = 26.1; (B) 1,3-CHD polymerized first, fractionation solution, PCHD wt % = 11.1.

Figure 13. SEC chromatograms from the synthesis of three-armed PCHD star: (A) PCHD arm, (B) first sampling (120 min), (C) unfractionated three-armed PCHD star, (D) fractionated three-armed PCHD star.

Figure 14. SEC chromatograms from the synthesis of three-armed PCHD star with end-capping: (A) PCHD arm, (B) 1,3-butadiene end-capped PCHD arm, (C) first sampling (60 min), (D) unfractionated three-arm PCHD star, (E) fractionated three-armed PCHD star.

Figure 15. SEC chromatograms from the synthesis of three-armed polybutadiene star: (A) PBD arm, (B) first sampling (15 min), (C) second sampling (60 min), (D) unfractionated three-arm PBD star.

Figure 16. SEC chromatograms from the synthesis of PS-PCHD three-arm star-block copolymer: (A) PS segment of the diblock arm, (B) PS-PCHD diblock arm, (C) first sampling (60 min), (D) unfractionated PS-PCHD three-arm star-block co-polymer, (E) fractionated PS-PCHD three-arm star-block copolymer (once).

Figure 17. SEC chromatograms from the synthesis of PCHD-PS three-arm star-block copolymer: (A) PCHD segment of the diblock arm, (B) PCHD-PS diblock arm, (C) first sampling (60 min), (D) unfractionated PCHD-PS

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three-arm star-block co-polymer, (E) fractionated PCHD-PS three-arm star-block copolymer four times.

Figure 18: TEM Micrographs of PS/PCHD Diblocks. The light regions are PS and the dark regions are PCHD stained with osmium tetraoxide. These specimens were prepared by solvent casting and annealing; shearing may be used to enhance long range order. (a) End on view of core-shell cylinders in band across the center of this image. (b) Side-on view of core-shell cylinders.

Figure 19. Crosslink PCHD.

Detailed Description

Polymerization of 1,3-CHD without Additives

1,3-CHD was polymerized using several anionic initiators under different conditions, and the results are summarized in Table 1. This table shows that the "traditional" anionic initiators, isomers of BuLi, do not work very well in controlling the polymerization of 1,3-CHD if used without additives. n-BuLi only produced trace amounts of polymer (not shown in Table 1); sec-BuLi, $tert$-BuLi, or phenyllithium gave better results (runs 1, 2, 9, and 10 in Table 1), but the molecular weights could hardly be manipulated and the polydispersities were quite large, as a low molecular weight tail is clearly seen in the SEC trace in Figure 1a. As polymerization continued, the molecular weight increased, but there was still a tail at the low molecular weight end of the distribution (Figure 1b). This indicates that some of the anionic chains failed to grow beyond the early stage of polymerization. It is generally agreed that anionic polymerization of 1,3-CHD is difficult to control because of side reactions. The side reactions during initiation are isomerization of the monomer to produce its 1,4-isomer and further to benzene; in some cases cyclohexene was detected. The main side reactions during chain propagation are chain transfer through proton elimination and chain termination via hydride abstraction, as shown in Figure A. Under anionic polymerization conditions (strong base), chain transfer through hydride elimination (reaction a) and/or allylic proton abstraction (reaction b) always compete with chain propagation (reactions c and d). 1,4-CHD, a very reactive chain-transfer agent for

alkyllithium-initiated polymerizations, is almost unavoidably produced during the course of polymerization. The ability of 1,4-CHD to decrease strongly the observed molecular weight in the lithium-naphthalenide-initiated polymerization of 1,3-CHD has been demonstrated. Lower polymerization temperatures also gave better results (runs 3 and 4 in Table 1), but poor solubility of the polymerization products under these conditions prevented further pursuit of this approach. Polymerization carried out in THF at low temperature also did not give the desired result (run 5 in Table 1). Since one of the possible side reactions involves hydride elimination, with the formation of stable lithium hydride (LiH) as the driving force, it is that using larger counterions such as potassium could minimize this process. This was indeed the case when benzylK, cumylK, or Naphthalene/K was used (Table 1, runs 6-8): the polydispersities were narrowed, but the molecular weights of these samples were always far lower than expected. Moreover, ^{1}H NMR data revealed that the ratio of vinyl protons to nonvinyl protons is much lower than the theoretical value (1 /3). Side reactions other than chain transfer or termination must be involved in these polymerization procedures.

Polymerization of 1,3-CHD with Additives

Additives play an important role in anionic polymerization. They have been widely used to control the microstructures of polydienes and minimize side reactions in acrylate polymerization. Several monodentate additives, and the associated results are listed in Table 2. THF and *sec*-BuOLi, popular additives used to disrupt aggregation in anionic polymerization, failed to give positive results (runs 1 and 2 in Table 2). This suggests that chain aggregation is not the main problem in the anionic polymerization of 1,3-CHD. The *sec*-BuLi/t-BuOK system, regarded as "second generation" super base, yielded polymers with reasonably narrow MWD (Table 2 run 3), but the molecular weights were much lower than anticipated. One possible reason is that the polymerization has to be carried out in THF at low temperature (-78°C), and chains could not grow very long due to solubility problems (high MW PCHD has limited solubility in THF; the solubility also depends on the

microstructure). Using *sec*-BuLi in THF/toluene (1/2 v/v) at -40°C, Zhang and Rubenstein selectively polymerized the styrene group in 4-(vinylphenyl)-1-butene to generate a polymer with a polystyrene backbone and functional butenyl side chains. See Zhang, H.; Ruckenstein, E. *Macromolecules* **1999**, *32*,

5 5495. However, their targeted molecular weight was only about 4000 g/mol. Not surprisingly, this system does not work well with 1,3-CHD (Table 2, run 4). Polydentate additives can change anionic polymerization processes dramatically due to their chelating effect. Natori and co-workers reported that the polymerization of 1,3-CHD using *n*-BuLi/TMEDA exhibits "living"

10 character and that the ratio of *n*-BuLi and TMEDA that gives living character is crucial. See Natori, I. *Macromolecules* **1997**, *30*, 3696. It is believed that chain propagation and side reactions are strongly affected by the extent of the polarization of the Li-carbon bond in PCHDLi, and chelating by TMEDA offers the proper Li-C polarization. The *n*-BuLi/TMEDA initiation system is

15 difficult to handle because the resulting polymers are difficult to dissolve in common solvents (Table 2, runs 5 and 6). Good results could only be achieved for low-MW targets. *n*-BuLi/PMDETA, similar to the *n*-BuLi/TMEDA initiation system, failed to produce materials with narrow poly-dispersities and predictable MWs (run 7 in Table 2). This is probably because PMDETA does

20 not chelate as effectively as TMEDA, since the former is more bulky and has an extra chelating site. Bulkiness alone may not be the sole reason for effective chelating since DABCO, also bulky, is quite effective as discussed below. Other polydentate additives, such as DABCO, DPPE, and DME, used in combination with certain butyl-lithium isomers produced PCHD samples with

25 relatively narrow MWDs and modest molecular weights as summarized in Table 2.

DME, a weak-chelating agent, can be used as an effective additive under carefully chosen conditions (Table 2, runs 10-12). The ratio of 1,4 to 1,2 addition in PCHD from this system is about 69/31. A group of PCHD samples

30 having reasonably well-controlled molecular weights were made from *n*-BuLi/DME, and the results are listed in Table 3 (runs 8-16). One typical SEC

trace of PCHD made using this initiating system is shown in Figure 2a. The polydispersities are quite narrow for low molecular weight samples, but at higher MWs narrow MWD materials are elusive, at least partially due to the poor solubility of the polymer. The three isomers of butyllithium in combination with DME or TMEDA yield striking differences in the polymerization processes. In contrast, the three butyllithium isomers in the presence of TMEDA give very similar results for the polymerization of styrene. With *n*-BuLi, the initiation process proceeds at the same rate as propagation, but with *sec*-BuLi and *t*-BuLi the initiation is faster than propagation. This alone should not cause the observed differences reported by Natori et al. in the polymerization of 1,3-CHD. Adequate data to allow elucidation of these differences were not presented. However, the very reactive species generated from *tert*-BuLi/TMEDA and *sec*-BuLi/TMEDA must undergo some detrimental reactions other than initiation and propagation. For DME, these differences are not surprising since DME has limited stability toward butyllithium. The protons in the β-positions are more acidic than that in TMEDA; thus, they are more readily abstracted followed by elimination. This process is fastest with *tert*-BuLi and slowest with *n*-BuLi. Lower temperatures also increase the stability of DME toward BuLi.

DPPE is also an effective additive. Some of the characteristics of PCHD obtained from BuLi isomers with DPPE are listed in Table 2 (runs 7-9). Better results could be achieved if the reactions were carried out under optimal conditions with regards to solvents, temperatures, and the amount of the additive (ratios of BuLi/DPPE). The 1,4 to 1,2 ratio of the PCHD from this polymerization system is about 57/43. DABCO, a bulky chelating agent, combined with *sec*-BuLi or *tert*-BuLi gives the best control over MW and polydispersity in the polymerizations of 1,3-CHD, as indicated in Table 2 (runs 13-15) and Table 3 (runs 1-7) (also Figure 2b). The resulting PCHD has a 1,4 to 1,2 additions ratio of 93/7. By chelating with DABCO, the C-Li bond in PCHDLi becomes strongly polarized, and consequently, chain propagations were facilitated while side reactions were minimized. The linearity of Mn with

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conversion is often used as an experimental criterion to document that a polymerization is living. Unfortunately, this type of plot will only detect chain transfer reactions; it is not sensitive to chain termination. Natori used this plot to demonstrate that the *n*-BuLi/TMEDA/1,3-CHD system is living. To test

5   whether there is any chain termination occurring during the polymerization process, 1,3-CHD was polymerized with *n*-BuLi/TMEDA or DME by sequential addition of the monomer. Figure 3 shows the SEC traces of PCHD obtained by this approach. After adding a second dose of monomer, the peak became significantly broader as shown in Figure 3b. This indicates that chain

10   termination reactions do occur, with both DME and TMEDA. The large low molecular weight tail suggests that the chain transferred species could reinitiate 1,3-CHD.

Block Copolymerization Using BuLi without Additives

         The successful control of the anionic polymerization of 1,3-CHD using

15   certain initiating systems, as described above suggests the possibility of making well-defined PS-PCHD diblocks of high molecular weights and having a wide range of compositions. Several initiating systems and different polymerization sequences can be employed in this work. The conditions used and the characteristics of the resulting polymers are listed in Table 4. When styrene

20   was polymerized by *sec*-BuLi in benzene followed by addition of 1,3-CHD without use of any additive, the PSLi initiated the polymerization of 1,3-CHD (Figure B (B)). The cross-propagation was accompanied by a color change from orange-red to yellow within 20 s. This simple procedure works well for making PS-PCHD block copolymers with short PCHD segments and thus low

25   PCHD content in the copolymer. As shown in Figure 4a, the SEC trace of a PS-PCHD diblock copolymer (wt % of 1,3-CHD = 5.4) is symmetrical and monomodal. However, when the targeted 1,3-CHD composition in the PS-PCHD block copolymer was high (>20%), this polymerization was not well-controlled, as indicated by the low molecular weight shoulder in the SEC

30   chromatogram (Figure 4c). These low MW byproducts arise from side reactions such as chain transfer and/or chain termination. Since 1,3-CHD can

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undergo several detrimental reactions under anionic polymerization conditions (strong base) in addition to the desired propagation, the maximum attainable composition of PCHD in the copolymers with high molecular weight (>10 000 g/mol) is restricted regardless of the initial monomer ratio. The low molecular weight contaminants can be removed easily by solvent (toluene)/nonsolvent (methanol) fractionation. These results are similar to those reported by Zhong and Francois and Zhou et al. Zhong, X. F.; Francois, B. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 411; Francois, B.; Zhong, X. F. *Makromol. Chem.* **1990**, *191*, 2743; Francois, B.; Izzilllo, S.; Iratcabal, P. *Synth. Met.* **1999**, *102*, 1211; Zhou, J. Ph.D. Thesis, The University of Alabama at Birmingham, 1996. On the basis of infrared spectra, Zhong and Francois reported that the low molecular weight shoulder was pure PCHD. Consequently, they claimed that the metalated monomer formed by chain transfer reinitiated the polymerization of 1,3-CHD. Conversely, it has also been found that the fractionated low molecular weight material contains substantial amounts of PS, as revealed by the ^{1}H NMR spectra shown in Figure 5. The peak around 5.6 ppm is from the cyclohexene ring, and the peaks from 6.2 to 7.2 ppm are from styrene units. This is not surprising, since the initiation and chain propagation rates in the PSLi initiated 1,3-CHD polymerizations are not fast enough to avoid the side reactions that lead to chain terminations. In addition to chain termination by hydride abstraction (one of the well-known chain-transfer reactions for this monomer), 1,4-CHD, which is always present at some level in 1,3-CHD under strong base conditions, is a very effective chain terminator. While the possible reinitiation to create PCHD homopolymer quantitatively on the basis of the data at hand cannot be ruled out, the spectrum in Figure 5 strongly suggests that this process does not play a major role in our studies. These results show that it is very difficult to prepare PS-PCHD samples with high 1,3-CHD content by sequential polymerization of styrene, and then 1,3-CHD, using *sec*-BuLi alone as initiator. Table 4 also gives the characteristics of block copolymers prepared by polymerization of 1,3-CHD with *sec*-BuLi in benzene followed by the addition of styrene (Figure B (A)). PCHDLi chains can initiate

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the polymerization of styrene very rapidly under these conditions, as demonstrated by the yellow color turning to red-orange instantly upon addition of styrene. SEC traces for products of this reaction are shown in Figure 6. The polymerization of 1,3-CHD initiated by *sec*-BuLi in the absence of additives does not proceed in a controlled manner. The PCHD blocks are moderately polydisperse (Mw/Mn>1.2), as are the final PCHD-PS diblocks. With a short PCHD block, the resulting PCHD-PS block copolymer is monomodal (Figure 3a). However, bimodal PCHD-PS is formed when the PCHD block is longer (higher molecular weight) (Figure 3d). It is difficult to remove the low molecular weight shoulder from this material by conventional toluene/methanol fractionation. This is probably because part of the PCHDLi was deactivated before all the monomer (1,3-CHD) was consumed, and toluene is not a very good solvent for the PCHD block. More importantly, these results show that PCH-DLi can rapidly initiate the polymerization of styrene in hydrocarbon solvents even without the use of polar additives. This is in stark contrast to the copolymerization behavior of styrene and acyclic dienes.

When styrene and butadiene are simultaneously added to anionic initiators in hydrocarbon solvents, tapered block copolymer are formed because of the differences in reactivity ratios. Therefore, a "random" copolymerization behavior for styrene and 1,3-CHD can be anticipated. Francois et al. found similar behavior in *sec*-BuLi/cyclohexane initiation system. See Mr. Yunan Wan for his technical support. Francois, B.; Izzilllo, S.; Iratcabal, P. *Synth. Met.* 1999, *102*, 1211. Therefore, *sec*-BuLi was used to polymerize styrene and 1,3-CHD simultaneously in benzene at room temperature. The composition of the polymerization products was monitored by ^{1}H NMR as a function of polymerization time, and the results are summarized in Figure 7. The monomodal character of the polymerization products as evidenced by SEC traces (Figure 8, solvent: THF) strongly suggests that they are not simple mixtures of PCHD and PS homopolymers. From Figure 7, one can see that the 1,3-CHD content in the polymerization products reached a rather high level quickly (30.5 mol % of 1,3-CHD in 20 min and 34.3 mol % in 120 min).

Under these reaction conditions, all the monomer was consumed in about 4 h. The composition does not change much after 120 min, and it is always slightly lower in 1,3-CHD content than anticipated on the basis of the monomer charge ratio. This is likely caused by the above-mentioned side reactions, which also

5   consume some 1,3-CHD. These findings suggest that the rate of reaction of PSLi with 1,3-CHD in benzene at room temperature is comparable to that of PCHDLi with styrene. Natori reported the copolymerization behavior of 1,3-CHD with styrene in cyclohexane using the *n*-BuLi/TMEDA (4/5) initiating system at 40°C. See Natori, I.; Inoue, S. *Macromolecules* 1998, *31*, 982. He

10   found that styrene was preferentially polymerized in the initial stage, and the polymerization of 1,3-CHD started only when most of the styrene was consumed. The higher reactivity of styrene in their study may be attributed to the presence of TMEDA, which can change the polymerization behavior dramatically because of its strong chelating effects with the growing chain

15   ends. Attempts to determine the sequence distribution in the copolymers by NMR were not successful because the spectra were very complex.

The MALDI-TOF-MS spectrum of the polymerization product from the first sampling of the "random copolymerization" is shown in Figure 9a along with a spectrum of a PS-PCHD diblock with similar composition (Figure 9b).

20   The single peak around 6000 g/mol and the monomodal SEC traces (Figure 9) suggest that the copolymerization was of a statistical nature. The drastic intensity differences in the two spectra are noteworthy. It was consistently observed that the MALDI-TOF-MS signals for PS-PCHD block copolymers are very weak. A possible reason for the low response of PS-PCHD block

25   copolymers in MALDI-TOF-MS spectra is that effective MALDI requires that individual polymer chain be dispersed in matrix crystals. PCHD segments are rather rigid and tend to aggregate during the preparation of MALDI samples. Consequently, only a small portion of the PS-PCHD chains can be ionized. However, the intensity for the "random copolymerization" product is much

30   higher than that for PS-PCHD diblock copolymers. This also implies that the styrene and 1,3-CHD units are statistically distributed in the former copolymer

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(i.e., not blocky), making aggregation of PCHD more difficult. Furthermore, the rates of crossover reactions from PCHDLi to styrene and vice versa were comparable for the *sec*-BuLi/benzene system based on visual observations (as noted above). Using the naphthalene/potassium initiation system in THF at

5   -78°C, PCHD-PS-PCHD and PS-PCHD-PS triblock copolymers were successfully obtained with monomodal molecular weight distributions; however, the MWDs are rather broad (runs 10 and 11 in Table 4).

Block Copolymerization Using BuLi with Additives.

As discussed above, *sec*-BuLi alone does not polymerize 1,3-CHD in a

10   controlled manner in hydrocarbon solvents. Therefore, it is difficult to synthesize PS-PCHD block copolymers with high molecular weights and covering a broad compositional range, as is necessary for morphological studies, using this approach. The use of certain additives can improve the situation. As shown in Table 4 (run 3), a small amount of THF can have a

15   favorable impact on block copolymer formation via polymerization of 1,3-CHD followed by the addition of styrene. However, further attempts to target higher 1,3-CHD compositions and higher molecular weights were not successful because THF does not adequately suppress the side reactions. Moreover, THF may react with *sec*-BuLi at the polymerization temperature

20   used. Natori reported that the *n*-BuLi/TMEDA initiating system could polymerize 1,3-CHD in a "living" manner. 1,3-CHD and styrene was sequentially polymerized using this initiator system; theses results are listed in Table 4 (runs 4 and 5) and Figure 10. When styrene was polymerized first, the SEC trace exhibited a tail at high molecular weight (Figure 10a). On the other

25   hand, a low molecular weight shoulder was observed in the SEC chromatogram when 1,3-CHD was polymerized first (Figure 10b). The shoulder may arise from deactivated PCHDLi. In contrast to our findings, Natori reported that PCHDLi "living" chains could continue to grow by adding either styrene or 1,3-CHD. See Natori, I. *Macromolecules* **1997**, *30*, 3696; Natori, I.; Inoue, S.

30   *Macromolecules* **1998**, *31*, 982. However, tailing can be seen clearly in some of their published SEC chromatograms. A peak with extremely high molecular

weight (~1.3 million g/mol based on calibration with PS standards) was observed for many of the diblocks regardless of which monomer was polymerized first. Upon decreasing the solution concentration and repeating the SEC experiments, these peaks shifted to lower molecular weight (about 970 kg/mol calibrated with PS), and the fraction of the high molecular weight peak also decreased. When SEC experiments were run in $CHCl_3$, higher molecular weight peaks were also observed, but the positions moved to lower molecular weight (~500 kg/mol, based on calibration with PS). Variations of the molecular weight and the fraction of high and low molecular weight components upon changing the polymer concentration or the SEC solvent suggest that micelles exist in solutions of some of these PS-PCHD block copolymers. As discussed, the *n*-BuLi/DME or *sec*-BuLi/DABCO initiating systems can polymerize 1,3-CHD in a controlled manner with regard to molecular weight and Mw/Mn. Thus, it is natural to try to extend those approaches to the synthesis of PS-PCHD diblock copolymers. Typical results are listed in Table 4 (runs 9-12), and characterization data are given in Tables 5 and 6. Under these reaction conditions, PCHDLi efficiently initiates the polymerization of styrene and vice versa, as shown in Figure 11. When the targeted composition for PCHD was lower than 30 wt %, the resulting PS-PCHD block copolymers were unimodal, and the polydispersities were low (Mw/Mn < 1.1). However, a shoulder corresponding to the first block was always seen in the SEC traces of the diblocks when the composition of PCHD was higher than 30 wt %. If styrene was polymerized first, this low molecular weight shoulder could be removed easily by solvent/nonsolvent fractionation (toluene/methanol), and it mainly contained PS as revealed by ^{1}H NMR (Figure 12b). The compositions can be calculated from the intensities of styrene (6.2-7.2 ppm, 5H) and 1,3-CHD (5.4-5.8 ppm, 2H) repeating units. This is because 1,3-CHD terminated some PSLi and/or PS-PCHDLi chains. On the other hand, the low molecular weight shoulder was very difficult to remove by toluene/methanol fractionation if 1,3-CHD was polymerized first. The shoulder was probably formed by the self-termination of the PCHDLi chains,

since the possibility of PCHDLi chains being terminated by styrene is low. The difficulty in removing the low molecular weight component by toluene/methanol fractionation probably arises from the poor solubility of PCHD in toluene. The fractionation solution (supernatant) of a PS-PCHD block copolymer (1,3-CHD polymerized first) contained a significant amount of PS (Figure 12a, peaks from 6.2 to 7.2 ppm), which indicates inefficient fractionation. However, the possibility of PS being formed by the polymerization of styrene initiated by the metalated 1,3-CHD species (the latter formed by chain transfer) cannot be excluded.

Star Polymers

The synthesis of the 3-arm PCHD homo-star polymers was performed according to Figure C. The key step of this synthetic route was the linking procedure. It was anticipated that the PCHDLi chain end, without end-capping with 1,3-BD, was sufficiently bulky that steric hindrance would prohibit its complete reaction with the linking agent, CH_3SiCl_3. However, this reaction did yield three-arm star, although it required long reaction times (up to 2 weeks) as shown in Figure 13. The two-armed intermediate is clearly seen in the SEC trace of the first sampling. The possibility that some coupled material remains in the final product due to the limitations of SEC separation; however, the star peak is quite symmetrical cannot be excluded. When the PCHDLi anions was capped with several 1,3-BD units, the chain ends became much less bulky and the linking reaction took place much faster, as shown in Figure 14. The linking reaction was so fast under the reaction conditions that the two-arm intermediate could not be detected after only 15 min of reaction. One possible reason for this very rapid linking reaction is that the additive, DABCO, also functions as a promoter. To check this hypothesis, 1,3-BD was polymerized using *sec*-BuLi in benzene and linked the resulting anions with CH_3-$SiCl_3$ in the presence of DABCO. The condensation reaction proceeded quickly; no two-arm material was detected even at the first sampling (after 15 min of reaction), as shown in Figure 15. Even though the linking reaction was allowed to continue, it was virtually finished in 1 h, as can be seen by comparing the SEC traces at 1 h and

1 day (Figure 3c,d). Tsiang found, consistent with these results, that the linking efficiency of (PB)₃SiCl with PS-PBLi was promoted from ~ 30% without a polar additive to >90% with a polar additive in 10 min. See Tsiang, R. C. C. *Macromolecules* 1994, *27*, 4399. The large arm peak was from the

5   large excess of arm anions used in this experiment. The molecular characteristics of the resulting star polymers are summarized in Table 7. The measured molecular weights of the arms (weight-average molecular weight) are higher than those of the predicted (number-average molecular weight) probably because some initiators were killed by some impurities in the reactor.

10   From Table 7 it can be seen that both arms and fractionated stars had very narrow molecular weight distributions (Mw/Mn < 1.1), indicating that the final star material is homogeneous.

Solvent (toluene)/nonsolvent (methanol) fractionation was used to remove the extra arm from the final three-armed PCHD star, and this proved to

15   be difficult as shown in Figure 14E (also Figure 13D). This may arise from the modest molecular weights of the PCHD materials investigated. The polymer precipitate and solution phase separation of a polymer in the solvent/nonsolvent system depend on its molecular weight. The higher the molecular weight, the easier the phase separations and hence the higher the

20   fractionation efficiency. However, there was one factor that prevented a pursuit of PCHD star homopolymers with higher molecular weight: polymers of 1,3-CHD are difficult to dissolve in common organic solvents if the molecular weight is high (>30 000 g/mol). A block-copolymer arm composed in part of polystyrene should improve the solubility.

25   The star-block copolymers were synthesized as shown in Figure D. Several star-block copolymers with both PS and PCHD as the outer blocks were synthesized, and the molecular characteristics of those polymers are summarized in Table 8. Molecular weights determined by light scattering and by MALDI-TOF-MS are in excellent agreement with one another if one

30   considers that the former value is a weight-average and the latter a number-average molecular weight. Both SEC and the absolute methods confirm very

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narrow molecular weight distributions for the star-block materials. The initial steps for these syntheses involved the preparation of living block copolymers that could be linked to make the desired star-block copolymers. For the arms with PS as the outer block, the polymerization of 1,3-CHD using the living

5   polystyrene chain as initiator has proven to be feasible. It has been reported that the polymerization rate of 1,3-CHD initiated by PSLi is faster than that by BuLi. The progress of the synthesis for one (PS-PCHD)$_3$SiCH$_3$, as monitored by SEC, is shown in Figure 16. The monomodal nature of the PS block and PS-PCHD arm indicates their homogeneity. The small amount of coupled

10   product seen in the chromatogram of the PS-PCHD arm is due to termination of the sample with methanol containing air. The linking reactions are very similar to these of PCHD three-arm star as discussed above. Excess arm can be removed by solvent/nonsolvent fractionation. However, if the targeted PCHD composition was too high, the monomer (1,3-CHD) was not consumed quickly.

15   Over time, a small portion of 1,3-CHD molecules may isomerize to its 1,4-isomer, which can terminate some of the living chains (PS-b-PCHDLi). Such "dead polymer" can be removed easily by solvent/nonsolvent fractionation. The key to the synthesis of stars with PCHD as the outer block, (PCHD-PS)$_3$SiCH$_3$, is an efficient crossover reaction from PCHDLi to styrene. This

20   reaction was previously demonstrated to be possible. It was also found that the sec-BuLi initiated polymerization of 1,3-CHD and styrene simultaneously resulted in random copolymers, which indicated the comparable cross reaction rate. Francois and co-workers also reported the quasi-alternate nature of the synchronized polymerization of styrene and 1,3-CHD using BuLi. See

25   Francois, B.; Lartigau, C.; Da Cunha, L. J. Chim. Phys. 1998, 95, 1226. Figure 17 shows the SEC chromatograms of one of the (PCHD-PS)$_3$SiCH$_3$ (run 5 in Table 8). The PCHD block shows a symmetric peak, but the PCHD-PS arm has a small peak at the low molecular weight end, which corresponds to the PCHD block as shown in Figure 17. There is no such problem when the

30   molecular weight of the PCHD block is low (<10 000 g/mol). This indicates that the crossover reaction from PCHDLi to styrene is not 100% complete

when the PCHD block is very long. In this case, the 1,3-CHD polymerization takes longer to attain high molecular weight PCHD, and during this time some PCHDLi can be terminated or undergo chain transfer. These transferred species are not reactive enough to initiate styrene. Moreover, it is very difficult

5 to remove this small peak by fractionation using toluene/methanol as the solvent/nonsolvent. This may be because toluene is not a good solvent for PCHD of high molecular weight. Under careful experimental condition, the unwanted lower molecular weight components can be fractionated away by using chloroform (as solvent) and hexane (nonsolvent). These results indicate

10 that the PCHD chains are stiff. 46 Thus, these star-block copolymers are expected to have interesting morphological properties since they have both architectural asymmetries (star architecture) and conformational asymmetry (stiff chain).

Nanostructures

15 Applicants previously synthesized poly(styrene-block-cyclohexadiene) and collaborated on a study of the morphology of self-assembled, microphase-separated diblock copolymer of PS and PCHD. An unusual core-shell cylinder-in-cylinder morphology not previously found in neat diblock copolymers was observed in three different specimens of different molecular

20 weights but all having similar composition (about 37% by volume PCHD). This structure consists of hexagonally packed cylinders of PCHD dispersed in a PS matrix; in the center of each PCHD cylinder there is a PS cylinder (Figure 18). This structure is the precursor to the novel nanotubes that are the subject of this proposal; by removing the PS inside and outside the PCHD cylinder,

25 PCHD nanotubes may be produced.

The first synthesis of crosslinked polymer nanotubes from block copolymers was described by Guojun Liu in early 2000. See S. Stewart, G. Liu, "Block Copolymer Nanotubes", *Angew. Cherm. Int. Ed., 39,* 340 (2000). His group made these materials by ozone induced degradation of a

30 polyisoprene phase within cylindrical micelles formed from an ABC triblock terpolymer. These nanotubes are acrylate based, and they will thus lack the

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high strength and thermal stability inherent in poly(phenylene) materials. Nevertheless, inspired by their elegant work, the present invention is directed to the core-shell cylinder-in-cylinder morphology that was observed for PS/PCHD diblocks as a means to synthesize functional polymer nanotubes.

5   To be able to remove the PS blocks it is necessary to have cleavable linkages connecting the two chain segments in the block copolymers. Such diblock copolymers can be synthesize by esterification of hydroxyl groups placed at one end of the PCHD chains with carboxylic acid groups placed at one end of the PS chains (see Figure E). The chemistries to be used for chain

10   end functionalization (carboxylation of PS chain ends with CO_2 and reaction of PCHD chain ends with ethylene oxide) are based on well-established literature procedures. For example, reaction of PCHD anions with ethylene oxide followed by protonation creates the desired end functionalized PCHD, while reaction of PS anions with CO_2 under appropriate conditions yields the

15   complementary end reactive PS. The compositions of the materials is controlled at about 37 vol % PCHD, since this is the composition that yielded cylinder-in-cylinder morphologies for three PS-PCHD diblocks, having different molecular weights. The diameter of the nanotubes is controlled by the molecular weight of the PCHD block.

20   Nanotubes are formed by casting films of the diblocks annealing and or using shearing to orient the dispersed cylinders, photocrosslinking of the PCHD phase, hydrolysis of the ester linkages under acidic conditions, and washing out of the PS material with solvents. The processing conditions controls the extent of long range order present in the microphase separated

25   structure and can be used to control the aspect ratio – and thus properties – of the nanotubes. THF or dioxane containing aqueous acid may be used for hydrolysis. This solvent system will swell the polymer phases permitting cleavage of ester linkages to occur. The removal of the PS phase, especially the PS inside the PCHD nanocylinders, requires careful solvent selection to

30   preferentially swell the crosslinked PCHD domains. It will also be possible to carry out a partial hydrolysis in such a manner as to create a "nanotube brush"

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(nanotubes projecting out from a surface in the z direction). PCHD can be aromatized using p-chloranil or the more efficient reagent 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. These nanotubes have hydroxyl groups on their surface due to cleavage of the ester linkages. These groups are then used to

5   attach things to the nanotubes or to promote interactions between the nanotubes and some matrix in which they are dispersed. These surfaces are above be chemically modified to create a wide range of tunable surface chemistries.

Applicants note some difficulty in removing all the PS from the interior of the PCHD tubes. However, if this problem is encountered, one option is to

10   aromatize the PCHD and then remove the PS by pyrolysis (polyphenylene is extremely thermally stable). This strategy was previously used to create a non-equilibrium "honeycomb morphology" from a PS/PP block copolymer. It is also possible that the aromatization reaction will not occur throughout the PCHD phase but only near the surface. This may prove to impart adequate

15   properties to the nanotubes. However, it is also possible that thermal treatment (pyrolysis) of these tubes, similar to the manner by which poly(acrylonitrile) in converted to conventional carbon fibers, might yield unique and useful nanotubes.

Nanotubes based on this block copolymer precursor approach are

20   intermediate in diameter to single-walled carbon nanotubes and lipid tubules, with diameters ranging from about 10-100 nm and controlled through block copolymer molecular weight (MW), composition, and optional addition of homopolymer. Their lengths can be controlled over the range of tens to many thousands of nm, giving them controllable and potentially very long aspect

25   ratios. Compared to other nanotubes, these materials are inexpensive to manufacture, amenable to scale up, and ordered arrays on a surface may be readily created through self-assembly. In addition, the synthesis route will yield products with controlled surface functionality. Both conducting and non-conducting materials can be generated. In addition to the synthesis of

30   nanotubes, the general synthetic approach described herein could also be used

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to synthesize PP nanocylinders (nanowires after doping), nanospheres (a new type of quantum dot), or sheets of nanoscale thickness.

Other morphologies (spheres, cylinders, or lamellae of PCHD) could also be obtained appropriate choice of composition of PS/PCHD block copolymers. Morphological characterization is a key step in any effort to relate nanoscale structure to properties. The core-shell PS-PCHD block copolymers and the nanotubes produced from them are characterized via transmission electron microscopy (TEM), field emission gun scanning electron microscopy (FEGSEM), and small angle scattering experiments. For observation of the PS-PCHD diblock core shell morphology prior to hydrolysis and nanotube formation, Cryoultramicrotoming will be used to produce ultra thin sections approximately 300-800 Å thick. Staining with OsO_4 allows TEM imaging of the nanoscopic PCHD hollow tubes, which have self assembled onto a hexagonal lattice (34). Small angle scattering experiments are performed in order to accurately determine the lattice symmetries and dimensions of the morphologies. Control of nanotube size via control of molecule weight and composition will be confirmed by microscopy and scattering; it is important to employ a combination of both TEM and scattering techniques in the determination of morphological structure since the two techniques compensate for each others weaknesses. SAXS (X-ray) can be done using a rotating anode sources and a two-dimensional area detector at the University of Massachusetts.

After hydrolysis and nanotube formation, the dispersed nanotubes are deposited on amorphous carbon substrates for imaging via TEM and electron diffraction characterization of crystallinity in cases where the structures are converted to PP. The nanotubes are then imaged via FEGSEM which is capable of resolving structures of 4 nm without need of metal coatings. In cases where the tubes are doped to provide enhance electrical conductivity, characteristic X-ray detectors on both the TEM and FEGSEM instruments will allow spatially resolved mapping of elemental composition variations. Atomic force microscopy will also be used to observe the nanotubes. AFM provides a

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convenient means of accurately measuring tube dimensions, and mechanical properties of individual tubes can be probed by applying pressure with the AFM tip.

The proposed structures have a number of exciting optical device applications as well as uses as nanoprobes and in field emission. Ordered two-dimensional arrays of the nanotubes may be made by solvent etching of a surface having the cylinders oriented perpendicular to the surface. Nanolithographic patterning may be performed by selective masking during the UV irradiation step. The ordered tubes can be selectively filled with desired materials, e.g. metals. Other architectures besides tubes (nano-cylinders, -plates) can also be made based on cylindrical or lamellar morphologies. These molecular objects can be useful for miniaturization of optical and electrical devices and micromechanical systems (MEMS). Surface initiated polymerization (SIP) can be utilized to grow PCHD polymer, patterned or non-patterned, on surfaces. By combining microcontact printing and dip-pen nanolithography with SIP, PCHD precursor polymer brushes can be grown as arrays and subsequently aromatize these structures. These materials will exhibit interesting electrical and optical properties that can potentially benefit the display and semiconductor industries.

Numerous studies could be performed with scanning probe microscopy. These range from high-resolution morphological characterization of the nanotubes themselves to more exotic measurements including attaching or growing a nanotube on the tip of a cantilever. This will enable experiments the user can functionalize the apex of the nanotube with a specific molecular species and probe a companion surface to measure molecule-molecule interactions. An AFM tip with a nanotube attached has also been shown to enhance resolution for imaging molecules on surfaces. Other applications include growing the nanotubes between the apex of two cantilever tips and measuring the mechanical properties of the nanotubes.

This application foresees the ability to grow a nanotube that is itself piezoelectric in nature. There have been some recent developments in

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piezoelectric copolymers, but these have been bulk materials. It would be very significant if one can produce a PP nanotube that produces piezoelectric voltage when bent or can be induced to move in specific ways when a voltage is applied. Nanomachines and nanoelectronic devices would evolve quickly from such structures.

Experimental Procedures

PCHD Synthesis

Materials. Benzene (Fisher, >99%), cyclohexane (Fisher, >99%), THF (Aldrich, 99.9%), and methylcyclohexane (Aldrich, 99%) were purified according to the anionic polymerization standards, as described in the literature. TMEDA (Aldrich, >99%), N,N,N',N',N'-pentamethyldiethylenetriamine (PMETE-DA, Aldrich, 99%), DME (Acros, >99%), and 1,2-dipiperidino-ethane (DPPE, Sigma, >99%) were stirred over freshly crushed CaH_2 powder for at least 24 h and distilled from potassium (K) mirror twice and finally from potassium/sodium alloy under high vacuum. Naphthalene (Aldrich, >99%) and 1,4-diazabicyclo[2.2.2]octane (DABCO, Aldrich, 98%) were sub-limed under high vacuum three times and then diluted in cyclohexane and benzene, respectively. Potassium *tert*-butoxide (*t*-BuOK, Aldrich, 95%) was diluted in THF, and phenyllithium (PhLi, Aldrich, 1.8 M in ether and cyclohexane) and *tert*-butyllithium (*t*-BuLi, Aldrich, 1.5 M in pentane) were used as received. 1,3-CHD (Aldrich, 97%) was cleaned by treating over CaH_2 followed by exposure to sodium mirrors at room temperature 2-3 times for 24 h each. This "roughly" purified 1,3-CHD was finally treated with n-BuLi or dibutylmagnesium (MgBu2 Aldrich, 1.0 M in heptane) at 0°C for 30 min just before the polymerization. Butyllithiums (sec-BuLi and n-BuLi) were prepared by reactions of the corresponding butyl chloride with lithium powder in hexane under vacuum. Cumyl potassium (CumylK) and benzyl potassium (BenzylK) were made via published methods.

Polymerization and Characterization. All polymerizations were performed under high vacuum using custom-made glass reactors. Break-seals allowed introduction of reagents sequentially, and constriction seal-offs

permitted intermittent removal of products. The molar ratio of additive to initiator was from 1.5 to 3 unless otherwise stated. In a typical polymerization experiment, about 75 mL of pure benzene was distilled into a reactor with all the purified reagents attached via break-seals. The reactor was removed from the vacuum line after evacuation. Then about 4.3 mL of sec-BuLi (in hexane, 7 x 10^{-5} mol/mL) and 3.5 mL of DABCO (in benzene, 2.1 x 10^{-3} mol/mL) were introduced into the reactor. After stirring for 5 min at room temperature, 4.4 g (0.055 mol) of 1,3-CHD was added. The reaction was allowed to continue for about 6 h and terminated with degassed methanol. The polymer solutions were precipitated in a large excess of methanol with 2,6-di-$tert$-butyl-4-methylphenol (butylated hydroxytoluene, BHT) added to prevented oxidative degradation. The stabilized polymer was isolated by filtration and dried under high vacuum. Number-average molecular weights (Mn) and polydispersity indices (Mw/Mn, where Mw is weight-average molecular weight) were obtained from size exclusion chromatography (SEC) relative to calibration with polystyrene (PS) standards in either THF or chloroform (CHCl$_3$). SEC in THF (flow rate: 1 mL/min; Waters Styragel 100, 500, 10^3, 10^4, and 10^5 Å columns) was obtained using a Waters 510 pump equipped with a Waters 410 differential refractometer detector; SEC in CHCl$_3$ (flow rate: 0.3 mL/min; columns: Polymer Lab. PL-Gel 5 im MiniMIX narrow bore columns with pore size from 100 to 10^5 Å) was acquired from a Waters 2690 system with a Waters 2410 refractive index and a Waters 996 photodiode array detectors. Proton nuclear magnetic resonance (^{1}H NMR) experiments were carried out in CDCl$_3$ at 30°C using a Bruker ARX-300 instrument. The 1,2 to 1,4 ratios were determined from the relative areas of protons that are adjacent to the double bond (α position) and those in β positions. Each 1,2-unit has three α protons and three β protons, while a 1,4-unit has two α protons and four β protons. The Mn of the product of the polymerization described above is 20.1 kg/mol with a polydispersity of 1.04, as determined by SEC in THF.

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Block Co-polymers

Materials. All materials were purified to anionic polymerization standards, as reported in the literature, and brief procedures are described as follows. Benzene (Fisher, >99%) and hexanes (Fisher, ≥ 99.9%) were purified by stirring over concentrated sulfuric acid for 2 weeks, followed by drying over ground calcium hydride (CaH_2) on the vacuum line overnight. After degassing several times, these solvents were distilled into calibrated cylinders containing n-BuLi (Aldrich, 1.6 M in hexanes) and a few drops of styrene. The persistence of the bright orange color (polystyryllithium, PSLi) indicated the purity of the solvents. Tetrahydrofuran (THF, Aldrich, 99.9%) was refluxed over sodium for at least 6 h and collected into a flask containing sodium dispersion under argon. This flask was then connected to the vacuum line; the solvent was degassed and distilled into a flask with sodium/potassium alloy. After stirring for some time, the bright blue color that developed showed that the THF was free from impurities deleterious to anionic polymerizations. TMEDA (Aldrich, >99%) and DME (Acros, >99%) were purified using the same procedures as for THF except potassium (K, Aldrich, 98%) mirrors were used instead of sodium dispersion. Styrene (Aldrich, 99%) was dried over CaH_2 and finally distilled from dibutylmagnesium (Mg-Bu$_2$, Aldrich, 1.0 M in heptane) and collected in ampules using a short-path distillation apparatus. 1,4-Diazabicyclo[2.2.2]-octane (DABCO, Aldrich, 98%) was purified by sublimation three times under vacuum and then diluted in benzene or cyclohexane. Naphthalene was also purified by sublimation three times but diluted in THF. 1,3-CHD (Aldrich, 97%) was cleaned by treating over CaH_2, sodium mirror (3 times), and finally n-BuLi or MgBu$_2$. Butyllithium (*sec*-BuLi or n-BuLi) was prepared from the reaction of 2-chlorobutane (Aldrich, g 99%) or 1-chlorobutane (Aldrich, ≥ 99%) with lithium powder (Aldrich, high sodium, 99%) in hexane. Potassium naphthalenide was made by reacting naphthalene with a K mirror in THF at -78°C for 2 h just before polymerization.

Polymerization. All polymerizations were carried out under high vacuum using custom-made glass reactors, and detailed procedures are outlined in the literature. It is possible to synthesize PS-PCHD diblocks by either polymerizing 1,3-CHD first, followed by addition of styrene (Figure B, (A)), or by polymerizing styrene first, followed by addition of 1,3-CHD (Figure B, (B)). Both approaches were employed in this work. In a typical experiment to prepare PS-PCHD diblock copolymer, about 85 mL of purified benzene was distilled into an evacuated reactor with attached ampules containing all the necessary purified reagents. The reactor was removed from the vacuum line by heat-sealing after degassing. A 5.5 mL aliquot of sec-BuLi (9.7×10^{-5} mol/mL in hexanes) was added to the solution followed by 2.3 g (0.022 mol) of styrene. The polymerization started right away (deep red color) and was allowed to continue for 6 h before taking an aliquot (~ 1 mL) for characterization. Size exclusion chromatography (SEC) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) results indicated the molecular weight of the first block was 4.52 kg/mol with a polydispersity of 1.08. About 2.5 mL of DABCO (3.2×10^{-4} mol/mL in benzene) was introduced into the reactor through a break-seal. After stirring about 5 min at room temperature, 6.4 g (0.08 mol) of 1,3-CHD was then added from another ampule. The solution turned to golden yellow quickly and was allowed to continue to polymerize for another 6 h before terminating the reaction with degassed methanol. The final product was found to have a weight-average molecular weight (Mw) of 18.6 kg/mol (from multiangle laser light scattering (MALLS)), a number-average molecular weight (Mn) of 15.4 kg/mol (from MALDI-TOF-MS), a polydispersity (Mw/Mn) of 1.03, and a composition of PCHD with 66.0 wt % (from ^{1}H NMR). For a representative PCHD-PS diblock copolymer, about 90 mL of benzene was used as solvent. After stirring of 3.1 mL of sec-BuLi (9.7×10^{-5} mol/mL in hexanes) with 1.6 mL of DABCO (3.2×10^{-4} mol/mL in benzene) for 5 min at room temperature, 3.0 g (0.038 mol) of 1,3-CHD was added and the polymerization was continued for 6 h. A small aliquot (~1 mL) was taken to characterize the PCHD block

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before adding 4.4 g (0.042 mol) of styrene and allowing it to polymerize for another 6 h. The first block was found to have Mn of 11.7 kg/mol (MALDI-TOF-MS) with Mw/Mn = 1.11. The polymerization was stopped by adding degassed methanol. The final diblock copolymer had Mw of 41.8 kg/mol

5   (MALLS), Mn of 44.2 kg/mol (SEC), Mw/Mn of 1.07 (SEC), and a composition of PCHD of 39.4 wt % (from ^{1}H NMR). The polymer solutions were precipitated in a large excess of methanol with 2,6-di-tert-butyl-4-methylphenol (butylated hydroxytoluene, BHT) added as antioxidant. The final polymer was isolated by filtering and drying under high vacuum. For

10   some samples, solvent/nonsolvent fractionation (toluene/methanol) was used to remove homopolymer contaminants. Methanol was added slowly to the polymer solution in toluene (concentration ~ 0.5% w/v) until turbidity appeared. The solution was then heated gently while stirring to eliminate turbidity, and it was then transferred to a warm separatory funnel. This system

15   was kept undisturbed overnight to allow phase separation. This procedure was usually repeated until SEC could detect no undesirable products.

Characterization. SEC experiments in THF were carried out at 30°C using a Waters 510 pump and Waters 410 differential refractometer detector (flow rate: 1 mL/min; columns: Waters 100, 500, 10^3, 10^4, and 10^5 Å). SEC

20   experiments in chloroform (CHCl$_3$, flow rate: 0.3 mL/min) were done at 30°C on a Waters 2690 system with Waters 2410 refractive index and Waters 996 photodiode detectors. Two Polymer Laboratories 5 μm PL-gel MiniMIX narrow bore columns with pore size from 100 to 10^5 Å were used. This system was also connected to a Wyatt DAWN DSP MALLS detectors equipped with 5

25   mW linearly polarized He-Ne laser (wavelength) 632.8 nm). The MALLS unit has 18 detectors with fixed detector angles from 22° to 147°. To calculate the absolute molecular weight, dn/dc values of the samples are required. The refractive index increments (dn/dc) for PCHD and PS in CHCl3 were measured with a Brice-Phoenix differential refractometer, operating at 632.8 nm and

30   calibrated with aqueous potassium chloride solutions. ^{1}H NMR experiment was carried out in CDCl3 at 30°C using a Bruker ARX 300 instrument.

MALDI-TOF-MS spectra were obtained with a PerSeptive Biosystems Voyager Elite DE instrument using linear mode. A 20 kV acceleration was used with delayed extraction. The spectra were collected by summing 250 shots by using a nitrogen laser (337 nm, 3 ns pulse width) operated at 5 Hz.

5   Samples were prepared by mixing matrix (dithranol, ~ 10 mg/ mL) and ionizing salt (silver trifluoroacetate, ~ 1 mg/mL) with polymer species (~ 1 mg/mL) in a ratio of 20/20/1 (v/v). $CHCl_3$ was the solvent. Approximately 0.5 μL of the sample solution was applied to the sample plate. All spectra were baseline corrected and smoothed. Peptide standards were used to calibrate the

10   instrument externally.

Star Polymers

Materials. All materials were purified to anionic polymerization standards as reported in the literature, and brief procedures were described as follows. Benzene (Fisher, >99%) and hexanes (Fisher, $\geq$ 99.9%) were purified

15   by stirring over concentrated sulfuric acid for 2 weeks followed by drying over grounded calcium hydride (CaH_2) in a vacuum line overnight. After degassing several times, they were distilled into calibrated cylinders containing n-BuLi (Aldrich, 1.6 M in hexanes) and a few drops of styrene. The persistence of the bright orange color (polystyryllithium) indicated the purity of the solvents.

20   Tetrahydrofuran (THF, Aldrich, 99.9%) was refluxed over sodium for at least 6 h and collected into a round flask containing sodium dispersions under argon. This flask was then connected to the vacuum line; the solvent was degassed and distilled into a flask with sodium/potassium alloy. After stirring for some time, the bright blue color showed that the THF was free from impurities

25   deleterious to anionic polymerizations. 1,3-Butadiene (1,3-BD, Aldrich, $\geq$ 99%) was condensed in a flask containing freshly grounded CaH2 at -78°C and connected to high-vacuum line. After stirring at -10°C for 2 h, the monomer was distilled into another flask containing sodium chunks and stirred for 30 min at -10°C. The monomer was then exposed to n-BuLi for 30 min at -10°C,

30   collecting the desired amount into calibrated ampules, and diluted with purified hexanes. Styrene (Aldrich, 99%) was dried over CaH_2 and finally distilled

from dibutylmagnesium (MgBu2) and collected in ampules using short-path distillation apparatus. 1,4-Diazabicyclo[2.2.2]octane (DABCO, Aldrich, 98%) was purified by sublimation three times under vacuum and then diluted in benzene or cyclohexane. 1,3-CHD (Aldrich, 97%) was cleaned by treating over CaH_2, sodium mirror (three times), and finally n-BuLi or MgBu2, and the details was described elsewhere. 28 sec-Butyllithium (sec-BuLi), prepared from the reaction of sec-butyl chloride (Aldrich, $\geq$ 99%) with lithium powder in hexane, was used as the initiator. Methyltrichloro-silane (CH_3SiCl_3, United Chemical Technologies, Inc., $\geq$ 99.9%) was stirred over CaH_2 overnight, followed by fractional distillation on the vacuum line (collecting the middle 1/3 fraction) and then subdivided into ampules. It was diluted to the desired concentration with purified hexane.

Polymerization. All polymerizations were carried out under high vacuum using custom-made glass reactors with sec-BuLi/DABCO (1/2) as the initiating system and benzene as the solvent. Detailed procedures are outlined in the literature. PCHD-PS and PS-PCHD arms were made by sequential addition of monomers. Following the completion of each polymerization stage, an aliquot was taken for characterization. In a typical experiment, about 90 mL of purified benzene was distilled into a high-vacuum evacuated reactor with attached ampules containing all the necessary purified reagents. The reactor was removed from the vacuum line after degassing. Then 3.8 mL of sec-BuLi (1.23 x 10^{-4} mol/mL in hexanes) and 2.5 mL of DABCO (2.8 x 10^{-4} mol/mL in benzene) in ampules were introduced into the reactor through break-seals. After stirring about 5 min at room temperature, 4.6 g (0.058 mol) of 1,3-CHD was added. The polymerization started right away (golden yellow color) and was allowed to continue for about 6 h. An aliquot (~1 mL) was taken, and SEC results indicated the MW of the arm was 13.6 kg/mol (calibrated with polystyrene standard) with MWD) 1.05. After end-capping the PCHD living chains with about 0.2 mL of butadiene, the linking reaction started by adding 2.9 mL of CH_3SiCl_3 (4.6 x $10._5$ mol/mL in hexanes). The linking process was monitored by taking aliquots on a scheduled basis and checking with SEC.

After the linking reaction was completed, degassed methanol was added to terminate the excess arm. The polymer solutions were precipitated in a large excess of methanol with 2,6-di-tert-butyl-4-methylphenol (butylated hydroxytoluene, BHT) added. The final polymer was filtered and dried under high vacuum. After fractionation, the Mw of the three-arm PCHD star from the polymerization described above is 41.2 kg/mol with a MWD of 1.06 as determined by SEC equipped with a multiangle laser light scattering (MALLS) detector.

Solvent/nonsolvent (toluene/methanol) fractionation was used at room temperature to remove the excess unreacted arm material. Methanol was added slowly to the polymer solution in toluene (concentration ~ 0.5% w/v) until turbidity appeared. The solution was heated gently to eliminate turbidity while stirring. It was then transferred to a warm separatory funnel. This system was left undisturbed overnight to allow phase separation. This procedure was repeated as necessary.

Characterization. SEC experiments in THF were carried out at 30°C using a Waters 510 pump and Waters 410 differential refractometer detector (flow rate: 1 mL/min; columns: Waters 100, 500, 10^3, 10^4, and 10^5 Å). SEC experiments in chloroform ($CHCl_3$, flow rate 0.3 mL/min) were done at 30°C on a Waters 2690 system with Waters 2410 refractive index and Waters 996 photodiode detectors. Two Polymer Laboratories 5 μm PL-gel MiniMIX narrow bore columns with pore size from 100 to 10^5 Å were used. This system was also connected to a Wyatt DAWN DSP MALLS detectors equipped with 5 mW linearly polarized He-Ne laser (wavelength) 632.8 nm). The MALLS unit has 18 detectors with fixed detector angles from 22° to 147°. To calculate the absolute MW, dn/dc values of the samples are required. The refractive index increments (dn/dc) for PCHD and PS in $CHCl_3$ were measured with a Brice-Phoenix differential refractometer, operating at 632.8 nm and calibrated with aqueous potassium chloride solutions (dn/dcPS) 0.172 mL/g and dn/dcPCHD) 0.125 mL/g). The dn/dc for the star-block polymers were calculated from the weighted average dn/dcstar) xPS(dn/dc)PS + (1 - xPS)(dn/dc)PCHD, where

xPS is the PS weight fractions determined by ^{1}H NMR. The ^{1}H NMR experiment was carried out in CDCl$_3$ at 30°C using a Bruker ARX 300 instrument. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were obtained with a PerSeptive Biosystems Voyager Elite DE instrument using linear mode. 20 kV acceleration was used with delayed extraction. The spectra were collected by summing 250 shots by using a nitrogen laser (337 nm, 3 ns pulse width) operated at 5 Hz. Samples were prepared by mixing matrix (dithranol, ~ 10 mg/mL) and ionizing salt (silver trifluoroacetate, _ 1 mg/mL) with polymer species (~1 g/mL) in a ratio of 20/20/1 (v/v). CHCl3 was the solvent. Approximately 0.5 µL of the sample solution was applied to the sample plate. All spectra were baseline corrected and smoothed. Peptide standards were used to calibrate the instrument externally.

Any patents or publications mentioned in this specification are indicative of the level of those skilled in the art to which the invention pertains. These patents and publications are herein incorporated by reference to the same extent as if each individual publication was specifically and individually indicated to be incorporated by reference.

The present examples along with the methods, procedures, treatments, molecules, and specific compounds described herein are presently representative of preferred embodiments, are exemplary, and are not intended as limitations on the scope of the invention.

While the foregoing description was directed to the preparation of some particular materials, it will be understood that in view of the teaching presented herein, one of skill in the art could readily prepare a variety of modified viral materials, all of which are within the scope of the present invention.

We claim:

Table 1 Polymerization of 1,3-CHD Using Various Anionic Initiators (without additives)

Run	Initiator	Solvent/Temp (°C)	[CHD] mole/L	[I] $\%10^3$ mole/L	Yield %	$M_{n, Cal}$ $\%10^{-3}$	$M_{n, SEC}$ $\%10^{-3}$	M_w/M_n (SEC)
1	s-BuLi	Benzene/20	0.53	1.40	53	29.9	7.6	2.17
2	s-BuLi	Benzene/20	0.59	4.69	59	9.9	7.3	1.49
3	s-BuLi	Ben./Hex./0 [a]	1.04	5.56	68	15.0	13.1	1.22
4	s-BuLi	MeCyclohex./-70 [b]	0.88	3.51	83	20.0	18.8	1.43
5	s-BuLi	THF/-78	1.00	7.36	47	10.9	5.1	4.92
6	BenzylK	THF/-78	1.45	2.63	93	44.1	26.0	1.38
7	CumylK	THF/-78	1.29	5.75	89	17.9	15.1	1.30
8	Naphthalene/K	THF/-78	1.09	6.99	98	25.0	17.4	1.40
9	t-BuLi	Benzene/20	1.05	3.65	75	5.8	9.5	2.07
10	t-BuLi	Benzene /20	1.14	9.96	49	9.1	7.1	1.77
11	PhLi	Benzene/20	1.05	3.04	71	27.6	10.6	2.06

Table 2 Polymerization of 1,3-CHD using BuLi with Additives

Run	Initiator	Solvent/Temp (°C)	Additive	[Add.]/ [I]	[CHD] mole/L	[I] %10³ mole/L	Yield %	$M_{n, Cal}$ %10⁻³	$M_{n\ SEC}$ %10⁻³	M_w/M_n (SEC)
						Mono-dentate Additive				
1	s-BuLi	Benzene/0	THF	19.2	1.02	8.16	37	10.0	2.2	4.28
2	s-BuLi	Benzene/20	s-BuOLi	1.5	0.82	2.20	78	30.1	4.97	2.21
3	s-BuLi	THF/-78	t-BuOK	2.9	1.18	4.86	57	19.4	3.6	1.19
4	s-BuLi	Toluene/-40 [a]	THF		0.97	5.55	23	13.9	3.6	1.77
						Poly-dentate Additive				
5	n-BuLi	Cyclohexane/40	TMEDA [b]	1.21	0.70	5.99	100	9.3	18.4	1.38
6	n-BuLi	Cyclohexane/40	PMDETA [b]	1.27	0.81	2.62	100	24.6	27.9	1.61
7	n-BuLi	Benzene/20	DPPE [b]	2.33	1.05	8.35	100	10.1	5.1	1.07
8	s-BuLi	Benzene/20	DPPE	3.02	1.14	7.80	92	11.7	NOT Soluble	
9	t-BuLi	Benzene/20	DPPE	3.09	1.04	7.65	88	10.9	NOT Soluble	
10	n-BuLi	Benzene/0	DME [b]	4.43	0.58	6.00	98	7.7	11.3	1.07
11	s-BuLi	Benzene/20	DME	4.80	1.09	3.38	16	25.9	6.3	4.73
12	t-BuLi	Benzene/20	DME	4.71	1.75	6.80	9	20.6	4.9	3.18
13	n-BuLi	Benzene/20	DABCO [b]	3.19	0.90	5.08	94	14.2	37.8	1.24
14	s-BuLi	Benzene/20	DABCO	2.47	0.79	4.29	100	14.6	20.1	1.04
15	t-BuLi	Benzene/20	DABCO	1.54	1.15	5.18	87	17.8	17.6	1.11

Table 3 Poly(1,3-Cyclohexadiene) Homopolymers from BuLi and DABCO or DME

Run	[Additive]/[I]	[CHD](mole/L)	[I] %10^3 (mole/L)	$M_{n,Cal}$ %10^{-3}	$M_{n,SEC}$ %10^{-3}	M_w/M_n (SEC)
			s-BuLi/DABCO/Benzene / 20°C			
1	1.4	1.68	35.11	3.8	4.4	1.06
2	1.7	1.20	12.63	7.6	9.1	1.05
3	1.8	1.13	9.52	10.5	13.8	1.03
4	2.5	0.79	4.29	14.7	20.1	1.04
5	2.0	0.82	2.84	23.1	27.8	1.12
6	2.3	1.14	3.10	29.5	36.0	1.31
7	2.1	1.21	2.10	46.3	42.9	1.34
			n-BuLi/DME/Benzene/0°C			
8	1.7	1.04	17.6	4.7	4.0.	1.13
9	2.39	0.69	6.0	7.1	11.3	1.07
10	1.45	1.05	12.2	9.5	13.8	1.12
11	1.65	1.63	8.91	13.7	17.9	1.21
12	2.09	0.77	2.87	16.3	21.1	1.19
13	1.75	1.75	7.35	19.0	28.2	1.24
14	2.15	1.18	3.28	28.7	36.5	1.51
15	1.74	1.77	3.60	39.4	42.9	1.43
16	4.89	0.95	1.51	50.2	Not soluble	

Table 4 Characteristics of PS-PCHD Block Copolymer form BuLi with Various Additives

Run	Additive	[Add]/[I]	[ST] mole/L	[CHD] mole/L	[I] %10[-3] mole/L	$\bar{M}_n$[a] %10[-3]	Mw/Mn[a]	Comp.[b] wt% PCHD	Remarks
1[c]	No additive		0.449	0.646	2.78	22.7	1.22	38.4	St first
2[c]	No additive		0.321	0.777	15.4	8.0	1.25	70.7	CHD first
3[c]	THF	16.8	0.294	0.266	4.13	15.8	1.15	43.7	St first
4[d]	TMEDA	1.25	0.551	1.083	3.52		Multi-modal		CHD first
5[e]	TMEDA	1.27	0.637	0.625	3.47	23.7	1.09	45.1	St first
6[e]	TMEDA	1.33	0.803	1.015	8.53		bimodal		CHD first
7	Naphth./K/THF/-78°C		0.737	0.620	11.15	19.3	1.25		St first
8	Naphth./K/THF/-78°C		0.656	0.959	8.01	23.4	1.41		CHD first
9[f]	DME	5.71	0.240	1.354	7.01	27.0	1.04	82.2	St first
10[f]	DME	5.60	0.321	0.900	5.52	33.2	1.07	81.5	CHD first
11[g]	DABCO	1.74	0.719	0.539	4.88	6.21	1.06	34.7	St first
12[g]	DABCO	1.63	0.564	0.501	5.47	44.2	1.07	39.4	CHD first

[a]: From SEC in THF; [b]: From ^{1}H-NMR; [c]: s-BuLi in benzene at room temperature; [d]: n-BuLi in benzene at room temperature; [e]: n-BuLi in Benzene at room temperature;

[e]: n-BuLi in Cyclohexane at 40°C; [f]: n-BuLi in benzene at 5°C; [g]: s-BuLi in Benzene at room temperature.

Table 5   Characteristics of PS-PCHD Diblock Copolymers from s-BuLi/DABCO/Benzene/20°C

Run	[ST] mole/L	[CHD] mole/L	[I] $\%10^3$ mole/L	M_n^a $\%10^{-3}$	Mw/Mn [a]	M_w^b $\%10^{-3}$	M_n^c $\%10^{-3}$	Comp.[d] wt% PCHD
1	0.673	0.542	8.33	15.3	1.03	19.3	17.0	38.2
2	0.492	0.340	4.02	26.7	1.06	32.9	28.4	52.7
3	0.719	0.539	4.88	22.9	1.03	26.1	23.8	34.7
4	1.05	1.23	7.00	16.9	1.03	18.6	15.4	66.0
5	1.07	0.225	7.38	15.7	1.04	17.7	16.5	11.4
6	0.175	1.64	10.64	17.1	1.04	21.9	19.1	85.1

[a]. From SEC;   [b]. from SEC-MALLS;   [c]. from MALDI-TOF-MS;   [d]. via ^{1}H-NMR in CDCl$_3$

Table 6   Characteristics of PS-PCHD Diblock Copolymer from n–BuLi/DME/Benzene/5°C

Run	[ST] mole/L	[CHD] mole/L	[I] $\%10^3$ mole/L	M_n $\%10^{-3}$ [a]	Mw/Mn [a]	M_w $\%10^{-3}$ [b]	M_n $\%10^{-3}$ [c]	Comp. wt% PCHD [d]
1	0.502	0.538	5.00	28.9	1.05	31.3	28.2	51.0
2	0.599	0.221	4.15	20.6	1.05	25.7	24.4	21.7
3	0.932	0.596	6.92	27.8	1.04	30.5	29.5	36.8
4	0.240	1.354	7.02	27.0	1.06	28.4	26.7	82.2
5	0.519	0.525	5.06	46.1	1.08	43.8		41.7
6	0.705	0.850	7.61	30.1	1.05	32.1	31.0	52.3
7	0.745	0.766	7.89	28.7	1.04	28.9	27.8	46.0
8	0.635	0.925	7.76	30.0	1.07	33.9	30.4	62.1
9	0.553	0.546	5.15	23.5	1.05	27.1	26.6	42.3

[a]: From SEC; [b]: from SEC-MALLS; [c]: from MALDI-TOF-MS; [d]: via ^{1}H-NMR in $CDCl_3$

Table 7 Characterization of 3-Armed PCHD Stars

Polymer	PCHD arm		3-Armed Star	
	M_w^a ($\times10^{-3}$)	M_w/M_n^b ($\times10^{-3}$)	M_w^a ($\times10^{-3}$)	M_w/M_n^b ($\times10^{-3}$)
KH5-033	7.3	1.04	21.4	1.06
KH5-041	5.8	1.07	18.3	1.05
KH5-051	13.6	1.05	41.2	1.06

[a]. From SEC-MALLS; [b]. From SEC

Table 8 Star-Block Copolymer Characteristics

Polymer	First block M_n [a] (×10⁻³)	First block M_w/M_n [b]	Block Copolymer M_n [a] (×10⁻³)	Block Copolymer M_w [c] (×10⁻³)	Block Copolymer M_w/M_n [b]	Wt % PCHD [d]	Star Block Copolymer M_w [c] (×10⁻³)	Star Block Copolymer d_n/d_c [e]	Star Block Copolymer M_w/M_n [b]
				Polystyrene as outer block					
KH5-057	9.8	1.02	14.8	15.7	1.03	26.8	46.2	0.160	1.04
KH5-062	2.3	1.08	15.5	15.7	1.08	80.4	47.3	0.136	1.04
KH5-067	5.6	1.04	13.9	15.3	1.06	54.0	43.9	0.148	1.05
				Poly(1,3-Cyclohexadiene) as outer block					
KH5-071	4.7	1.10	14.2	15.3	1.06	31.2	45.1	0.158	1.05
KH5-077	13.4	1.07	16.6	18.1	1.08	74.1	49.4	0.139	1.06
KH5-081	14.2	1.08	24.9	27.1	1.09	56.3	74.9	0.147	1.07

[a]: From MALDI-TOF-MS; [b]: via SEC; [c]: From SEC-MALLS; [d]: via ¹H-NMR; [e]: in ml/g and calculated from the weight composition and the d_n/d_c data for PS and PCHD in $CHCl_3$ (0.172 and 0.125 ml/g, respectively).

53

Claims

1   1.   A nanostructured formation process comprising the steps of:

2   polymerizing a diene under conditions suitable to yield a structure

3   having at least one dimension ranging from 1 to 100 nanometers.

1

1   2.   The process of claim 1, wherein polymerization of the diene

2   occurs in the presence of a second monomer to form a block copolymer.

1

1   3.   The process of claim 1, wherein polymerization occurs under

2   conditions suitable for the structure to self assemble.

1

1   4.   The   process   of   claim   1,   wherein   the   diene   comprises

2   cyclohexadiene.

1

1   5.   The process of claim 2, wherein the second monomer comprises

2   styrene.

1

1   6.   The process of claim 1, wherein polymerization occurs in the

2   presence of an additive.

1

1   7.   The process of claim 6, wherein the additive is selected from the

2   group consisting of TMEDA, DME, DABCO, and butyllithium.

1

1   8.   A nanostructure formed by the process of claim 1.

1

1   9.   The process of claim 1, wherein the structure is selected from

2   the group consisting of nanotube, star polymer, nanofiber, nanosphere and

3   brushes.

1

1   10.   A composite material incorporating the nanostructure formed by

2   the process of claim 1.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

(A)

(B)

FIGURE 9

Ve (ml)

FIGURE 10

FIGURE 11

FIGURE 12

FIGURE 13
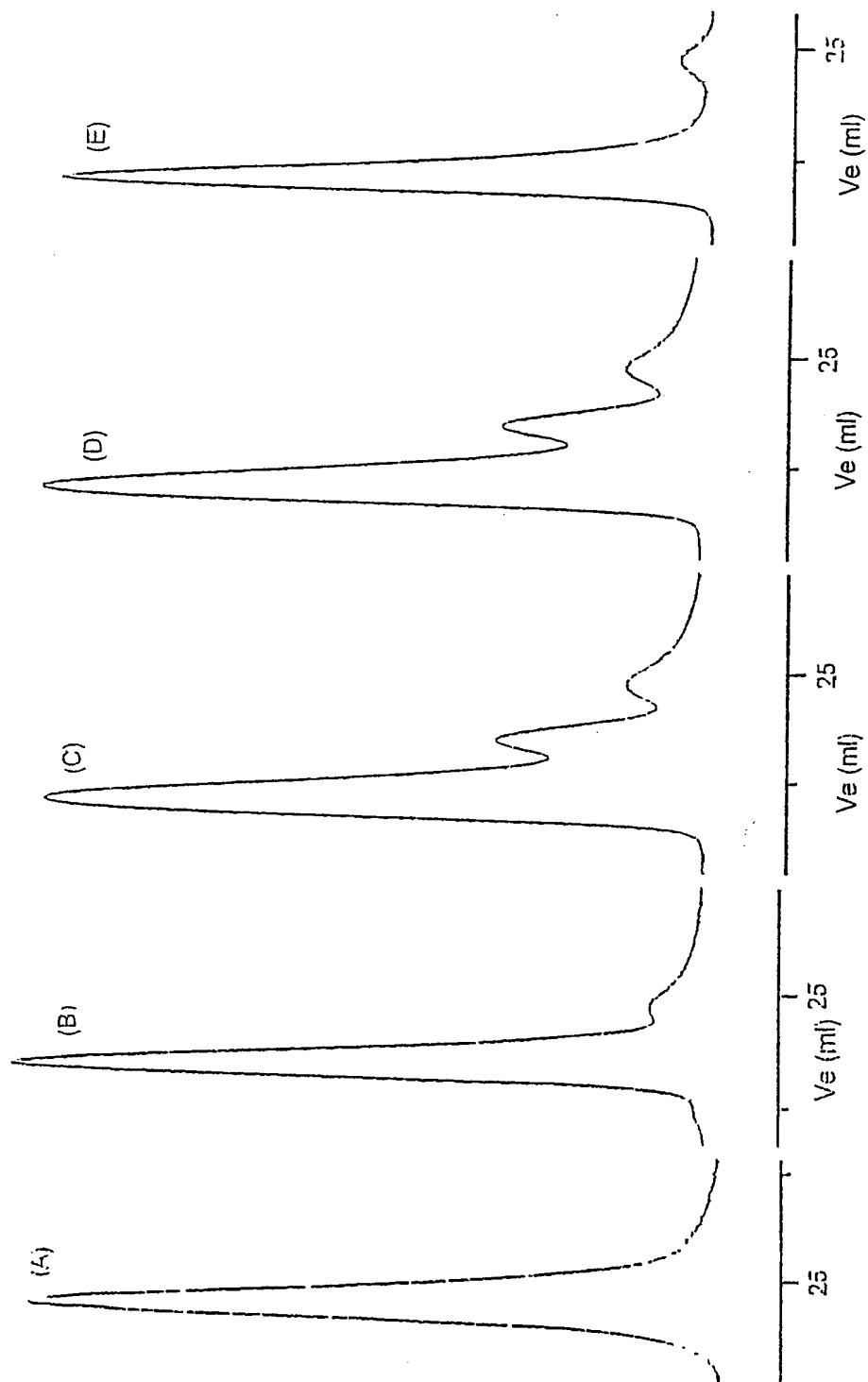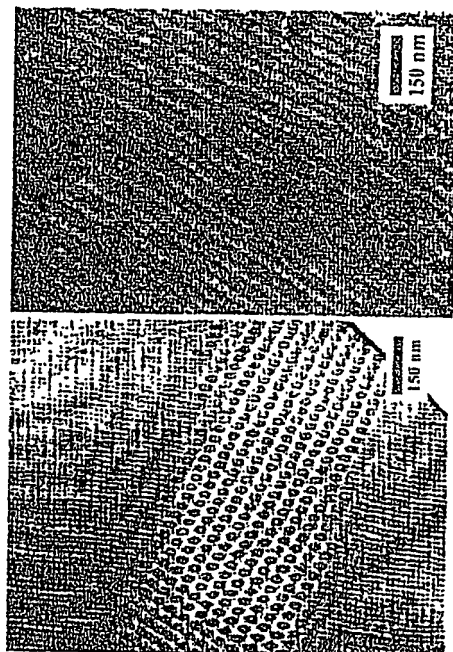
FIGURE 14

FIGURE 15

FIGURE 16

FIGURE 17

TEM Micrographs of PS/PCHD Diblocks. The light regions are PS and the dark regions are PCHD stained with osmium tetraoxide. These specimens were prepared by solvent casting and annealing; shearing may be used to enhance long range order. (a) End on view of core-shell cylinders in band across the center of this image. (b) Side-on view of core-shell cylinders.

(a)

(b)

FIGURE 18

1) Crosslink PCHD
2) Swell in solvent and hydrolyze ester linkage

3) Wash away PS phase

Crosslinked PCHD

PCHD phase

PS phase

FIGURE 19

(a) Hydride elimination (chain termination)

(b) Proton abstraction (chain transfer to monomer)

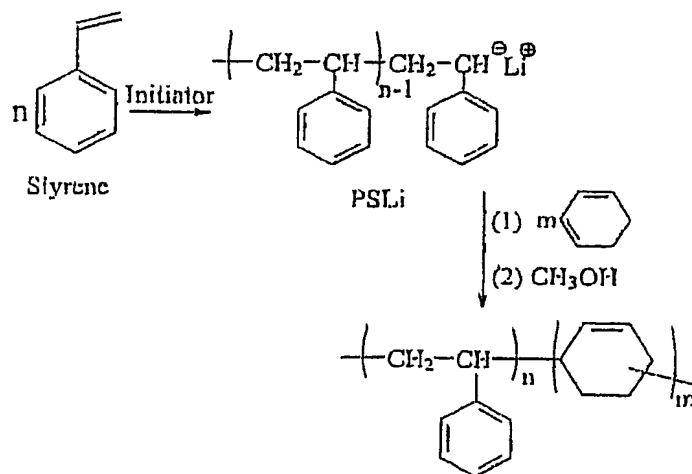(c) 1,4-addition and (d) 1,2-addition (chain propagations)

FIGURE A.3-0

(A)

PCHD-PS

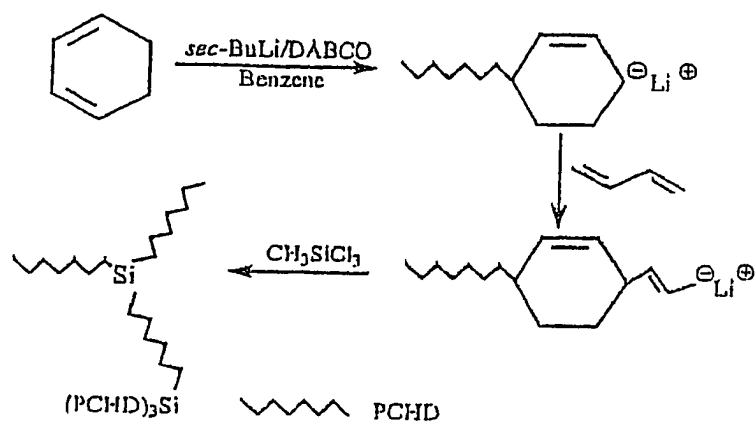(B)

FIGURE B-21

FIGURE 9.2

FIGURE 2-3

FIGURE 94

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7)   C08F 32/06, C08L 53/02
US Cl.   525/332.1, 328.8, 332.9, 333.1, 333.3, 526/308
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

US   525/332.1, 328.8, 332.9, 333.1, 333.3; 526/308

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST
search terms: diene, polymerization, nanometers, nanostructures

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,128,418 A (GRUBBS et al) 7 JULY 1992, col. 1, line 51, col. 10, lines 27 and 51	1, 3, 4
X	US 4,798,742 A (BALLARD et al) 17 JANUARY 1989, col.1, line 64, col. 2, line 55, col. 5, line 64	1, 3, 4, 6-8, 10

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex

* Special categories of cited documents

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Date of the actual completion of the international search	Date of mailing of the international search report
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(54) Title: NANOSTRUCTURES FORMED THROUGH CYCLOHEXADIENE POLYMERIZATION

(57) Abstract: A nanostructure formation process that includes the step of polymerizing a diene under conditions suitable to yield a structure having at least one dimension ranging from 1 to 100 nanometers. More specifically, the self-assembly of block copolymers of styrene and 1,3-cyclohexadiene is exploited to form a cylinder-in-cylinder morphology, followed by crosslinking of poly(cyclohexadiene) (PCHD) and removal of the polystyrene (PS) segments, as a means for producing novel functionalized PCHD nanotubes. PCHD may be aromatized to poly(phenylene) (PP), a strong, crystalline, and thermally stable engineering polymer. These materials characterized in terms of their sizes, shapes, surface chemistry and mechanical properties. Composites incorporating these nanotubes can be used in a new class of robust, lightweight, high strength materials.

NANOSTRUCTURES FORMED THROUGH CYCLOHEXADIENE POLYMERIZATION

Background

Field of the Invention

The present invention relates to the formation of nanostructures through polymerization reactions and, more particularly, to the formation of nanotubes through the controlled polymerization of cyclohexane.

Reference to Related Art

Synthesis of PCHD

Synthetic polymers are an indispensable and remarkably versatile class of materials. The suitability of a polymer for a particular application is controlled by its specific structural and molecular properties such as molecular weight (MW), molecular weight distribution (MWD), local and global architecture, and functionality. To understand the relationship between polymer structure and properties, there is great interest in well-defined polymers made by living addition polymerization processes. Tremendous progress has been achieved in living polymerizations over the past two decades, thanks to the development of new polymerization methodologies. Nevertheless, living anionic polymerization is still the most versatile technique for synthesizing polymers with well-defined structures. Many new materials with controlled architectures, functionalities, and narrow MWD have been made using anionic polymerization. However, most of the studies are limited to several well-behaved, mostly hydrocarbon, monomers (such as styrene, 1,3-butadiene, isoprene, etc.).

1,3-Cyclohexadiene (1,3-CHD) polymers (PCHD) are of interest from both scientific and practical standpoints. These polymers offer the opportunity to combine microstructural control during diene polymerization with post-polymerization chemistry in order to tailor the properties of the resulting polymers. PCHD and its derivatives should have higher mechanical strength and better thermal and chemical stability compared to common, i.e., vinyl, polymers due to the alicyclic structures (six-membered rings) in the main

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chain. PCHD can be modified by various dehydrogenation procedures, such as bromination followed by dehydrobromination, aromatization by p-chloranil, or catalytic dehydrogenation. The C=C bond in PCHD can also be hydrogenated by either diimide or using Pd/BaSO$_4$ under H$_2$ pressure. It has been reported

5   that hydrogenated PCHD has the highest Tg (231°C) of all hydrocarbon polymers. Hydrogenated PCHD polymers have good heat, weather, impact, abrasion, and chemical resistances, low water absorption, and birefringence; they also serve as good optical materials due to their excellent transparency and rigidity. The copolymer of 1,3-CHD with cyclopentadiene has been used as an

10   active element in photomicrolithographic devices, and the optical resolution is greatly enhanced by the addition of PCHD blocks. It has also been proposed that PCHD may be useful as a plastic material for undersea applications because of its high hydrolytic stability.

There have been many reports on the synthesis of PCHD polymers.

15   Essentially all conventional polymerization procedures have been applied to the polymerization of 1,3-CHD. These include cationic, radical, Ziegler-Natta, transition-metal complexes, and anionic polymerizations. Only low molecular weight or insoluble materials were obtained in most cases due to various side reactions. The anionic mechanism has proven to be the best way to polymerize

20   1,3-CHD with high conversion and molecular weight control, although side reactions, such as chain transfer and termination, have limited the maximum attainable molecular weight of PCHD. In general, the observed molecular weights are independent of conversion and do not depend on monomer or initiator concentrations under anionic polymerization conditions. The

25   formation of benzene, cyclohexene, and 1,4-cyclohexadiene (1,4-CHD) has been observed during polymerization. Using difunctional alkali naphthalenides as initiators, molecular weights as high as 19 kg/mol (Li +) and 38.7 kg/mol (Na +) were obtained in 1,2-dimethoxyethane (DME), in which the polymer precipitates. Very recently, Natori and co-workers reported that

30   polymerization of 1,3-CHD anionically could be controlled using certain additives. See Natori, I. *Macromolecules* **1997**, *30*, 3696; Natori, I.; Inoue, S.

Macromolecules **1998**, *31*, 982; Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*
4687.   They used the *n*-BuLi/N,N,N',N'-tetra-methylethylenediamine
(TMEDA) initiation system and carried out the reaction under nitrogen
atmosphere (pressure up to ~ 4 kg/cm^2) at 40°C. According to their findings,
the ratio of *n*-BuLi to TMEDA and the method of introducing the chemicals are
crucial for obtaining "well-controlled" PCHD (polydispersity indices < 1.1). A
family of PCHD homopolymers and their copolymers with styrene, butadiene,
and isoprene has been made using this method. However, all the samples with
narrow MWD were less than 15 kg/mol in molecular weight. Surprisingly,
other additives, even if structurally very similar to TMEDA, were found to be
less effective.

Block Co-Polymers

Block copolymers, composed of thermodynamically incompatible
blocks covalently bonded together, can self-assemble into well-ordered nano-
domains because of the mutual repulsions between unlike chain segments and
the constraints imposed by the connectivity of the blocks.   In the strong
segregation limit, even the simplest linear AB diblock copolymers consisting of
two flexible chains can exhibit a rich variety of morphologies depending on
their volume fractions. However, it is highly desirable to be able to control the
microphase morphology and the composition separately in actual applications.
Consequently, this dependence of morphology on composition limits flexibility
in designing new materials for specific usage.   For example, if a certain
purpose requires a material with a cylindrical morphology in which the
component comprising cylindrical domains makes up over 50 vol % of the
material, traditional neat block copolymers would not be useful.   In this
composition range only lamellar equilibrium morphologies will form for
typical diblock copolymers.

Two approaches have been used to uncouple this strict dependence of
block copolymer morphology on volume fraction.   One approach is to
introduce architectural asymmetry into the block copolymer (i.e., change the
connectivity of the different blocks).   Nonlinear architectures, such as

miktoarm stars and grafted block copolymers, have been demonstrated both theoretically and experimentally to allow control of morphology independent of the familiar composition windows found in linear AB diblock morphologies. For instance, PI (PI = polyisoprene) in a 3-miktoarm star of $(PI)_2PS$ (PS = polystyrene) with about 0.81 volume fraction of PS formed randomly oriented wormlike micelles dispersed in a continuous PS matrix. Moreover, this morphology was demonstrated to be the equilibrium state of the system. This unusual morphology is presumably due to the graft architecture of the molecule and the relationship between the particular volume fraction and the concavity of the PS/PI interface on which the two PI chains per molecule must reside. At the same volume fraction and molecular weight, a linear PS-PI diblock would have PI spheres distributed in PS matrix. Also, for a regularly spaced, tetrafunctional multigrafted block copolymer (PI backbone with double PS grafts) with ~ 9 vol % PS, instead of producing PS sphere/PS cylindrical structure as predicted by Milner's theory, an unusual new morphology was formed. The morphology can be described as a microphase-separated mesh of PS struts or wormlike domains in a PI matrix. These results clearly demonstrate the effectiveness of varying molecular architecture in "decoupling" the dependence between composition and morphology for block copolymers.

The alternate approach of introducing conformational asymmetry into the diblock copolymer has also attracted considerable interest recently. In a sense, common block copolymers can be best considered as flexible-semiflexible block copolymers due to conformational asymmetry reflecting differences in the statistical segment length (chain stiffness) of the blocks. Conformational asymmetry can shift the volume fraction range over which various morphologies are observed because of different space filling characteristics of the two blocks. AB diblock copolymers consisting of a flexible coil and a rigid rod block (so-called rod-coil block copolymers) represent the extreme case of conformational asymmetry. These materials have stimulated much research interest over the past decade, and a variety of

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supramolecular architectures have been observed for rod-coil block copolymer systems. The aggregation behavior of rod-coil systems reflects two different ordering phenomena: (i) the microphase separation of the coil and rod blocks into ordered periodic structures and (ii) the tendency of the rodlike block to

5　　　form anisotropic, ordered structures. Even though many fantastic structures have been observed, the phase behavior, and hence the properties, of rod-coil systems are difficult to tailor because of the complexities of the interactions in the system. However, if the stiffness of one block varies systematically while keeping the other block constant, the phase behavior could be tuned in a

10　　controlled manner. Lai et al. studied the phase separation of styrene-isoprene diblock copolymers and their hydrogenated derivatives (styrene-ethylene-*alt*-propylene and vinyl-cyclohexanes-ethylene-*alt*-propylene copolymers). See Lai, C.; Russel, W. B.; Register, R. A.; Marchand, G. R.; Adamson, D. H. *Macromolecules* **2000**, *33*, 3461. They found that the phase behavior did

15　　evolve as the conformational asymmetry parameter, ϵ, was varied, but not in a simple fashion. Gido, Mays, and their co-workers studied phase separation in polyisoprene-block-poly(*tert*-butyl methacrylate) (PI-PtBMA) diblock copolymers. For samples with volume fraction (Φ) > 0.30 of the "stiff" block, PtBMA, small phase boundary shifts were found, consistent with theoretical

20　　predications. See Pochan, D. J.; Gido, S. P.; Zhou, J.; Mays, J. W.; Whitmore, M.; Ryan, A. J. *J. Polym. Sci., Polym. Phys.* **1997**, *35*, 2629 and references cited therein. However, discrepancies were observed in the volume fraction dependence of experimentally determined morphological behavior Φ_{PtBMA} spherical micelles with weak lattice ordering in a PI matrix) and the

25　　theoretically calculated morphology (cylinder) when $\Phi_{PtBMA} < 0.30$.

Recently, there was observed an unusual core-shell cylinder-in-cylinder microphase-separated morphology for the polystyrene-block-poly(1,3-cyclohexadiene) (PS-PCHD) system, which may reflect their conformational asymmetry. This asymmetry might be expected given the fact that PCHD has

30　　para-linked cyclohexene rings incorporated into the main chain of the polymer.

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1,3-CHD polymers are a very interesting class of materials because of their unique structures and expected advantageous properties. Zhong and Francois synthesized PS-PCHD block copolymers using *sec*-butyllithium (*sec*-BuLi) in a nonpolar solvent by first polymerizing styrene, followed by addition

5   of 1,3-CHD to the living PS anions. See Zhong, X. F.; Francois, B. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 411; Francois, B.; Zhong, X. F. *Makromol. Chem.* **1990**, *191*, 2743; Francois, B.; Izzilllo, S.; Iratcabal, P. *Synth. Met.* **1999**, *102*, 1211. During polymerization of 1,3-CHD, they found that chain transfer to monomer was unavoidable and that some of the metalated monomer

10   reinitiated polymerization. They eventually converted the PCHD block to poly(p-phenylene) (PPP). Zhou also synthesized a series of PS-PCHD block copolymers using *sec*-BuLi. See Zhou, J. Ph.D. Thesis, The University of Alabama at Birmingham, 1996. He used benzene/hexane mixtures as the solvent (v/v = 9/1) and ran the polymerizations at low temperatures (<5°C) in

15   order to minimize side reactions. Even so, chain transfer and termination reactions limited the PCHD composition in the final products. Recently, Natori and co-workers reported that anionic polymerization of 1,3-CHD could be controlled using the *n*-BuLi/N,N,N',N'-tetramethylethylenediamine (TMEDA) initiator system. See Natori, I. *Macromolecules* **1997**, *30*, 3696; Natori, I.;

20   Inoue, S. *Macromolecules* **1998**, *31*, 982. Various block copolymers of 1,3-CHD with styrene, butadiene, and isoprene were made by sequential addition of the monomers. According to their findings, living PCHD (PCHDLi) and PS (PSLi) species have similar reactivity toward styrene, whereas PSLi chains hardly react with 1,3-CHD.

25   **Star Polymers**

Constituting the simplest form of branching, star polymers are ideal for investigation into the structure-property relationships of branched polymers. The first star polymers were synthesized in 1948 through condensation chemistry. Since then, virtually all polymerization methods have been used to

30   make various star polymers; however, all of these methods are variations of two more general methodologies. The first method involves the

polymerization of a monomer *"out of"* a multifunctional initiator. This can be an experimentally expedient and clean approach, but common practical difficulties with this method involve synthesis of an appropriate initiator and adequately promoting its efficiency. (To obtain narrow molecular weight distribution materials, all initiating sites must react quickly.) The second general method for making stars involves linking prepolymerized living polymer chains *"into"* a coupling reagent. This is by far the more extensively studied procedure. This latter approach provides the opportunity to sample and thus characterize the "arm" material before forming the star polymer and often allows mixed arm incorporation. Divinylbenzene (DVB) and chlorosilanes are the most popular linking agents used. Chlorosilanes have become the classic linking agents for the synthesis of star polymers using anionic polymerization. because of the clean and quantitative nature of the linking reaction (assuming steric effects are adequately considered). On the other hand, DVB provides robust but relatively less well-defined branched materials, since precise control over the number of arms is not possible and stars produced by this method are always mixtures of materials having different numbers of arms.

Compared to the number of publications on the synthesis and properties of star homopolymers, the number of studies published on star-block copolymers, which have block copolymer arms, is quite small. Price et al. synthesized three- and four-armed star-block copolymers of styrene and isoprene (with styrene as the outer block) using chlorosilanes as linking agents. See Price, C.; Watson, A. G.; Chow, M. T. *Polymer* 1972, *13*, 333. The styrene volume fractions of their samples were fixed at about 0.24. Even though about 25% excess of living arms was used, significant amounts of three-arm (for $SiCl_4$) and two-arm (for CH_3SiCl_3) species were formed. Bi and Fetters synthesized six- and nine-armed DVB-linked polystyrene-polyisoprene stars containing ~ 25 vol % polystyrene. See Bi, L. K.; Fetters, L. J. *Macromolecules* 1975, *8*, 90. This was achieved by adding a predetermined amount of DVB compounds to a solution of living diblock chains. Later, a variety of star-block copolymers with different kind of blocks have been

synthesized with this method. Extending their work, Bi and Fetters synthesized and studied two series of chlorosilane and DVB linked styrene-butadiene and styrene-isoprene star-block copolymers containing up to 29 arms and having approximately 27-40 vol % polystyrene (outer block). See Bi, L. K.; Fetters, L.

5   J. *Macromolecules* **1976**, *9*, 732. They found that the synthesis of four-armed star-block copolymers was facilitated by adding several units of butadiene to the polyisoprenyllithium chain ends prior to the addition of tetrachlorosilane. The linking of the diblock chains by DVB proceeded to virtual completion in benzene without a polar promoter or end-capping. Thomas, Fetters, and co-

10   workers studied a family of polystyrene-polyisoprene star-block copolymers (having up to 18 arms) made from the reaction of living diblock arms with chlorosilane linking agents. See Thomas, E. L.; Alward, D. B.; Kinning, D. J.; Martin, C. D.; Handlin, D. L., Jr.; Fetters, L. J. *Macromolecules* **1986**, *19*, 2197. A new equilibrium microdomain morphology, thought to be ordered

15   bicontinuous double-diamond (OBDD), was found in certain cases. Even though the nature of the morphology was subsequently reevaluated, the salient morphological features of star-block copolymers had been clearly demonstrated by this group. Inverse star-block copolymers, $(AB)_2Si(BA)_2$, with A = polystyrene and B = polyisoprene, were prepared by the chlorosilane

20   method using $SiCl_4$. In these materials, two arms were connected to the central silicon by their PS ends, and the other two arms were connected via their PI ends. The linking agent $SiCl_4$ was titrated with living (PI-b-PS) Li solution until two arms were linked to $SiCl_4$, as determined by size exclusion chromatography (SEC). The difunctional macromolecular linking agent was

25   then treated with a small excess of the living (PS-b-PI)Li solution to prepare the inverse star-block copolymer. The order of the addition was dictated by steric factors. Tsiang synthesized several four-armed stars with three polybutadiene arms and one polystyrene-block-polybutadiene arm, (PS-b-PB)Si(PB)$_3$. See Tsiang, R. C. C. *Macromolecules* **1994**, *27*, 4399. The key

30   step for this method is the successful synthesis of the pure $(PB)_3SiCl$ intermediate, which is obviously demanding. Molenberg and co-workers 18

synthesized four-armed polybutadiene-b-poly(diethylsiloxane) (PB-b-PDES) star-block copolymers by the reaction of living PB-b-PDES chains with 1,4-dimethyl-1,1,4,4-tetrachloro-1,2-disily-ethane. See Molenberg, A.; Moller, M.; Soden, W. *Acta Polym.* **1998**, *49*, 45. The star-block copolymers were cross-
5   linked by hydrosilylation of the PB double bonds with chloro-dimethylsilane followed by condensation of the chloro-silane groups with water. The resulting rubbers showed elastomeric behavior in tension and stress induced mesophase formation. All of the studies of star-block copolymer noted above focused on well-behaved monomers, mostly styrene, butadiene, and isoprene.

10   1,3-Cyclohexadiene (1,3-CHD)-based polymers are a structurally interesting class of material. With six-member alicyclic units in the main chain, a dramatic improvement of stabilities (thermal, chemical) and strength is expected in PCHD-based polymers. Through subsequent post-polymerization chemistry, such as aromatization or hydrogenation, PCHD can be converted to
15   other novel materials. Marvel and Hartzell polymerized 1,3-CHD using a Ziegler-Natta catalyst system and subsequently aromatized the polymer in 1959. See Marvel, C. S.; Hartzell, G. E. *J. Am. Chem. Soc.* **1959**, *81*, 448. Since then, essentially all the conventional polymerization methods have been used to polymerize 1,3-CHD. However, the best molecular weight and
20   conversions obtained were via anionic polymerization in hydrocarbon solvent. Copolymerization of 1,3-CHD with other monomers (styrene, isoprene, or butadiene) under various anionic conditions has also been investigated. Kara et al. very recently presented preliminary results of the synthesis of PCHD stars having up to 19 arms. To produce these materials, they synthesized PCHD
25   anions using *n*-BuLi/N,N,N'N'-tetramethylethylenediamine (TMEDA) and linked them using DVB.

Nanostructures

        There has been intense interest in nanostructured materials over the past few years, with much of the focus directed towards electronic applications, for
30   example, nanolithography. Nanotubes derived from carbon and "tubules" derived from phospholipids have also received a great deal of attention. The

former system is of fundamental interest as a true macromolecular system with a known architecture. Indeed, carbon nanotubes may be viewed as pure carbon fibers where the structure is entirely known to the atomic level, making them ideal materials for testing predictions of theoretical modeling. There is also

5   much interest in the practical properties of carbon nanotubes, due to their unique combination of dimension, structure, and topology. Key properties include: a large surface area that could be useful in mechanical and chemical applications, remarkable electronic properties (semiconducting or metallic), outstanding mechanical properties, and excellent thermal conductivity. Efforts

10   are underway to commercially exploit some of these properties. For example, the first single-molecule field-effect transistor has been built based on a single semi-conducting carbon nanotube. Self-assembly of carbon nanotubes into integrated assemblies could make nanotube electronics a practical reality. In terms of mechanical properties, elastic moduli of about 1000 GPa have been

15   measured for carbon nanotubes. There have been attempts to exploit carbon nanotubes as fillers in polymer composites, with some success, although lack of miscibility of the nanotubes with the matrix resin is a problem.

Lipid tubules are hollow phospholipid bilayer cylinders that are morphologically similar to a soda straw. They have lengths of tens or hundreds

20   of microns and diameters between 0.1 and 1 mm, making them very large relative to carbon nanotubes, which are several micrometers in length and 1-25 nm in diameter (larger sizes are for multi-walled species). To make lipid tubules useful in advanced materials applications, they may be metallized by coating with Ni or other metals; this imparts mechanical robustness and

25   conductivity to the tubules. These tubules may be used as "nano-vials" for controlled release of marine antifouling agents (release over many years) and controlled release of drugs (release over days to months). The metal clad structures also have interesting electromagnetic properties and are under investigation as miniaturized microwave circuits and as absorptive filters.

30   In addition to carbon and phospholipid nanotubes, there have been recent reports of nanotubes from metal oxides, amino acids, and organic

precursors. Despite the exciting scientific potential of these various types of nanotubes, they have serious practical limitations. For example, they are extremely expensive: purified single-walled carbon nanotubes cost about $2,000 per gram and the cost of lipid tubules is comparable. Also, it is difficult

5   to manufacture and purify the large amounts of these materials necessary for applications, although progress in scaling up single-walled carbon nanotubes is being made. Furthermore, there are limitations to the sizes that can be created, it is difficult to form ordered arrays, and the surface chemistries (important for functionalization and modifying surface interactions) are not readily

10   manipulated.

Block copolymers through self-assembly in bulk or in solution can form various nanostructures such as spheres, cylinders, vesicles, etc. Even nanotube formation has been reported for block copolymer systems by Eisenberg, although these tubes were not crosslinked and thus their stability is dependent

15   on their solvent environment. K. Yu and A. Eisenberg, "Bilayer Morphologies of Self-Assembled Crew cut Aggregates of Amphiphilic PS-b-PEO Diblock Copolymers in Solution" *Macromolecules*, *31*, 3509 (1998). Liu recently reviewed work in the area of nanostructures from "functional block copolymers", where a block is crosslinkable thus allowing the nanostructure to

20   be stabilized. Liu and his co-workers have synthesized various stabilized nanostructures including star polymers, nanospheres, tadpole molecules, crosslinked polymer brushes, and nanofibers. See G. Liu, "Nanostructures of Functional Block Copolymers", *Curr. Opinion Coll. Interface Sci.*, *3*, 200 (1998); J. Tao, S. Stewart, G. Liu, M. Yang, "Star and Cylinder Micelles of

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15   G. Liu, X. Xu, K. Skupinska, N. Hu, H. Yao, "Crosslinked Polymer Brushes Formation and Properties of Poly(isobutyl vinyloxy)ethyl cinnamate Brushes", *J. Appl. Polym. Sci., 53*, 1699-1707 (1994); G. Liu, L. Ciao, A. GtlO, "Diblock Copolymer Nanofibers", *Macromolecules, 30*, 5508- 5510 (1996). Recently, Stewart and Liu reported the first synthesis of crosslinked nanotubes derived

20   from block copolymers.   See S. Stewart, G. Liu, "Block Copolymer Nanotubes", Angew. Chem. Int. Ed., J2, 340 (2000). They prepared cylindrical nanocylinders of a poly(*tert*-butylacrylate-b-2-cinnamoylethyl methacrylate-b-isoprene) (PtBA-PCEMA-PI) triblock copolymer in methanol, followed by crosslinking of the PCEMA and removal of the inner PI block by ozonolysis.

25   Although this work represents a major advance, the synthesis of polymer nanotubes that have promise in opto-electronic applications and are strong and robust enough for structural applications (nanocomposites) and use as nanoprobes has not been reported.

With these nanotechnology applications in mind, the present invention

30   concerns the synthesis and characterization of a new type of nanotube based on self-assembled   block   copolymers   of   polystyrene   (PS)   and

poly(cyclohexadiene) (PCHD). PCHD is a structurally interesting polymer because it may be converted to poly(phenylene) (PP), a crystalline and chemically and thermally stable material, by aromatization. Furthermore, doping of PP will generate a conducting synthetic metal. Poly(phenylene) nanostructures have recently been reviewed. It is believed that PP "can adopt a pivotal role in synthesis-driven approaches toward molecular electronics since they combine the advantage of extended pi-conjugation with their ability to self-assemble into various supramolecular patterns." For example, ordering of PP chains into lamellar superstructures would lead to novel light emitting diodes. Use of PCHD as a precursor to PP will also avoid the major difficulty associated with synthesizing or processing high molecular weight poly(phenylene): it is an insoluble and intractable material. On the other hand, PCHD of high MW (> 30,000 g/mol) is soluble in some common organic solvents.

Summary of the Invention

The anionic polymerization of 1,3-cyclohexadiene (1,3-CHD) using various initiating systems and with or without additives is disclosed. In contrast to the situation with linear conjugated dienes, common anionic initiators in the absence of additives fail to produce poly(1,3-cyclohexadiene) (PCHD) with controlled molecular weight (MW) and narrow molecular weight distribution (MWD) because of side reactions. However, certain additives change the nature of the polymerization dramatically. Monodentate additives do not yield controlled polymerization, while some polydentate additives, such as N,N,N',N'-tetramethylethylenediamine (TMEDA), 1,2-dimethoxyethane (DME), and 1,4-diazabicyclo[2.2.2]-octane (DABCO), are effective in minimizing side reactions, if combined with the suitable butyllithium isomer. For example, the synthesis of PCHD samples with narrow MWD and good MW control is possible using the *n*-BuLi/DME/0°C or *sec*-BuLi/DABCO/20°C in benzene. The "living" character of these polymerizations is disclosed.

Additionally, the synthesis of block copolymers of 1,3-cyclohexadiene (1,3-CHD) and styrene under various conditions is disclosed. *sec*-Butyllithium

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alone can initiate the polymerization of 1,3-CHD but does not yield a living process due to chain transfer and termination reactions. However, certain additives such as tetramethylethylenediamine, dimethoxyethane, and 1,4-diazabicyclo[2.2.2]octane, combined with the suitable butyllithium isomer, can

5   be used to improve control of the polymerization of 1,3-CHD. Using these initiator systems, well-defined poly(styrene-block-1,3-cyclohexadiene)s with a wide range of compositions were synthesized and thoroughly characterized. In addition, the rate of crossover reactions during block copolymer formation and the "random" copolymerization of 1,3-CHD and styrene is disclosed.

10   The synthesis of well-defined, near-monodisperse, three-arm star and star-block copolymers based on poly(1,3-cyclohexadiene) (PCHD) is also disclosed. The stars were prepared by the reaction of living anionic chain ends of PCHD, poly(styrene-1,3-cyclohexadiene) (PS-PCHD), and poly(1,3-cyclohexadiene-styrene) (PCHD-PS) with CH_3SiCl_3 in benzene. 1,4-

15   Diazabicyclo[2.2.2]octane (DABCO) was used to control the anionic polymerization of 1,3-CHD; it also acted as a promoter during the linking reaction. The star polymers were fractionated to remove excess arm material and thoroughly characterized by size exclusion chromatography, matrix-assisted laser desorption ionization time-of-flight mass spectrometry, and light

20   scattering.

       Finally, the self-assembly of block copolymers of styrene and 1,3-cyclohexadiene is exploited to form a cylinder-in-cylinder morphology, followed by crosslinking of poly(cyclohexadiene) (PCHD) and removal of the polystyrene (PS) segments, as a means for producing novel functionalized

25   PCHD nanotubes. PCHD may be aromatized to poly(phenylene) (PP), a strong, crystalline, and thermally stable engineering polymer. These materials characterized in terms of their sizes, shapes, surface chemistry and mechanical properties. Composites incorporating these nanotubes can be used in a new class of robust, lightweight, high strength materials. By controlling molecular

30   weight and processing conditions, nanotubes of varying radius, wall thickness, and aspect ratio can be obtained. By varying the composition of the block

copolymer, other shapes besides tubes (cylinders, plates) can also be made. Reactive hydroxyl groups present on the surface of these molecular objects can be used to manipulate their processing characteristics and to provide strong bonding to matrix materials. The PP nanotubes may be insulating or they may be made conducting by doping. Such materials could also be used as a component in a smart composite designed to transmit an electronic signal if, for example, impacted by a projectile. Opto-electronic and nanoprobe applications are also envisioned for these materials.

Brief Description of the Drawings

Reference is made to the accompanying drawings, to wit:

Figure A. Possible Reactions of PCHD Anion with 1,3-CHD.

Figure B. Block copolymers prepared by polymerization of 1,3-CHD with *sec*-BuLi in benzene followed by the addition of styrene (A); Styrene polymerized by *sec*-BuLi in benzene followed by addition of 1,3-CHD without use of any additive, the PSLi initiated the polymerization of 1,3-CHD (**B**).

Figure C. The synthesis of star polymers.

Figure D. The synthesis of star polymers

Figure E. Synthesis of diblock copolymer of PS and PCHD with ester bond.

Figure 1. SEC traces of PCHD from sec-BuLi in benzene at 0°C: (a) polymerization time 2 h; conversion $\sim$ 43%; (b) polymerization time 6 h, conversion $\sim$ 51%.

Figure 2. SEC traces of PCHD from (a) n-BuLi/DME at 0°C, Mn = 11.3 kg/mol, Mw/Mn = 1.07; (b) sec-BuLi/DABCO at 20°C, Mn = 13.8 kg/mol, Mw/Mn = 1.03.

Figure 3. SEC traces of PCHD from n-BuLi/DME at 0°C: (a) aliquot from first dose of monomer, Mn = 18.4 kg/mol, Mw/Mn = 1.08; (b) aliquot from second dose of monomer, Mn = 19.7 kg/mol, Mw/Mn = 1.68.

Figure 4. SEC traces (eluent THF) of PS-PCHD from sec-BuLi in benzene (styrene polymerized first). (A) Monomer charge: styrene/1,3-CHD) 93/7 (mole); (a) Mn = 14 100 g/mol, Mw/Mn = 1.06. (B) Monomer charge:

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styrene/1,3-CHD = 53/47 (mole); (b) PS block, Mn = 15 100 g/mol, Mw/Mn = 1.04; (c) PS-PCHD block before fractionation, Mn = 22 400 g/mol, Mw/Mn = 1.22; (d) fractionated solution Mn = 16 400 g/mol, Mw/Mn = 1.07; (d) fractionated solid, Mn = 28 200 g/mol, Mw/Mn = 1.05.

Figure 5. ^{1}H NMR spectra of PS-PCHD SEC from sec-BuLi in benzene (a) before fractionation, PCHD wt %) 38.4; (b) after fractionation (solid), PCHD wt %) 43.1; and (c) after fractionation (solution), PCHD wt %) 12.9.

Figure 6. SEC traces (eluent THF) of PCHD-PS from sec-BuLi in benzene (1,3-CHD polymerized first). (A) Monomer charge: styrene/1,3-CHD) 35.2/64.8 (mole); (a) PCHD block, Mn = 5800 g/mol, Mw/Mn = 1.07; (b) PCHD-PS diblock, Mn = 10 100 g/mol, Mw/Mn = 1.09. (B) Monomer charge: styrene/1,3-CHD = 38.6/61.4 (mole); (c) PCHD block, Mn = 8100 g/mol, Mw/Mn = 1.13; (d) PCHD-PS block, Mn = 13 300 g/mol, Mw/Mn = 1.28. g/mol, Mw/Mn = 1.07; (b) third sampling, Mn = 13 200 g/mol, Mw/Mn = 1.11; (c) final product (6 h), Mn = 14 200 g/mol, Mw/Mn = 1.14.

Figure 7. Compositions of PCHD in PS-PCHD copolymer (from the polymerization of 1,3-CHD and styrene simultaneously using sec-BuLi in benzene) vs polymerization time.

Figure 8. SEC traces (eluent THF) of PS-PCHD from the polymerization of 1,3-CHD and styrene simultaneously using sec-BuLi in benzene: (a) first sampling, (20 min), Mn = 5600 g/mol, Mw/Mn = 1.07; (b) third sampling, Mn = 13 200 g/mol, Mw/Mn = 1.11; (c) final product (6 h), Mn = 14 200 g/mol, Mw/Mn = 1.14.

Figure 9. MALDI-TOF-MS spectra of PS-PCHD polymers: (A) "random" copolymer, Mn = 5900 g/mol, Mw/Mn = 1.03; (B) diblock copolymer, Mn = 15 400 g/mol, Mw/Mn = 1.01.

Figure 10. SEC traces (eluent THF) of PS-PCHD from n-BuLi/TMEDA/cyclohexane/40°C: (a) styrene polymerized first, Mn = 23 700 g/mol, Mw/Mn = 1.09; (b) 1,3-CHD polymerized first.

Figure 11. SEC traces (eluent THF) of PS-PCHD from sec-BuLi/DABCO/benzene: (A) styrene polymerized first: (a) PS block Mn = 8300 g/mol, Mw/Mn = 1.07; (b) PS-PCHD diblock before fractionation, Mn = 15 100 g/mol, Mw/Mn = 1.05; (c) PS-PCHD after fractionation, Mn = 15 300 g/mol, Mw/Mn = 1.03. (B) 1,3-CHD polymerized first: (d) PCHD block, Mn = 15 700 g/mol, Mw/Mn = 1.09; (e) PS-PCHD diblock before fractionation, Mn = 43 200 g/mol, Mw/Mn = 1.10; (f) PS-PCHD diblock after fractionation, Mn = 44 300 g/mol, Mw/Mn = 1.08.

Figure 12. ^{1}H NMR spectra of PS-PCHD SEC from sec-BuLi/DABCO/benzene: (A) 1,3-CHD polymerized first, fractionation solution, PCHD wt % = 26.1; (B) 1,3-CHD polymerized first, fractionation solution, PCHD wt % = 11.1.

Figure 13. SEC chromatograms from the synthesis of three-armed PCHD star: (A) PCHD arm, (B) first sampling (120 min), (C) unfractionated three-armed PCHD star, (D) fractionated three-armed PCHD star.

Figure 14. SEC chromatograms from the synthesis of three-armed PCHD star with end-capping: (A) PCHD arm, (B) 1,3-butadiene end-capped PCHD arm, (C) first sampling (60 min), (D) unfractionated three-arm PCHD star, (E) fractionated three-armed PCHD star.

Figure 15. SEC chromatograms from the synthesis of three-armed polybutadiene star: (A) PBD arm, (B) first sampling (15 min), (C) second sampling (60 min), (D) unfractionated three-arm PBD star.

Figure 16. SEC chromatograms from the synthesis of PS-PCHD three-arm star-block copolymer: (A) PS segment of the diblock arm, (B) PS-PCHD diblock arm, (C) first sampling (60 min), (D) unfractionated PS-PCHD three-arm star-block co-polymer, (E) fractionated PS-PCHD three-arm star-block copolymer (once).

Figure 17. SEC chromatograms from the synthesis of PCHD-PS three-arm star-block copolymer: (A) PCHD segment of the diblock arm, (B) PCHD-PS diblock arm, (C) first sampling (60 min), (D) unfractionated PCHD-PS

three-arm star-block co-polymer, (E) fractionated PCHD-PS three-arm star-block copolymer four times.

Figure 18: TEM Micrographs of PS/PCHD Diblocks. The light regions are PS and the dark regions are PCHD stained with osmium tetraoxide. These specimens were prepared by solvent casting and annealing; shearing may be used to enhance long range order. (a) End on view of core-shell cylinders in band across the center of this image. (b) Side-on view of core-shell cylinders.

Figure 19. Crosslink PCHD.

Detailed Description

Polymerization of 1,3-CHD without Additives

1,3-CHD was polymerized using several anionic initiators under different conditions, and the results are summarized in Table 1. This table shows that the "traditional" anionic initiators, isomers of BuLi, do not work very well in controlling the polymerization of 1,3-CHD if used without additives. *n*-BuLi only produced trace amounts of polymer (not shown in Table 1); *sec*-BuLi, *tert*-BuLi, or phenyllithium gave better results (runs 1, 2, 9, and 10 in Table 1), but the molecular weights could hardly be manipulated and the polydispersities were quite large, as a low molecular weight tail is clearly seen in the SEC trace in Figure 1a. As polymerization continued, the molecular weight increased, but there was still a tail at the low molecular weight end of the distribution (Figure 1b). This indicates that some of the anionic chains failed to grow beyond the early stage of polymerization. It is generally agreed that anionic polymerization of 1,3-CHD is difficult to control because of side reactions. The side reactions during initiation are isomerization of the monomer to produce its 1,4-isomer and further to benzene; in some cases cyclohexene was detected. The main side reactions during chain propagation are chain transfer through proton elimination and chain termination via hydride abstraction, as shown in Figure A. Under anionic polymerization conditions (strong base), chain transfer through hydride elimination (reaction a) and/or allylic proton abstraction (reaction b) always compete with chain propagation (reactions c and d). 1,4-CHD, a very reactive chain-transfer agent for

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alkyllithium-initiated polymerizations, is almost unavoidably produced during the course of polymerization. The ability of 1,4-CHD to decrease strongly the observed molecular weight in the lithium-naphthalenide-initiated polymerization of 1,3-CHD has been demonstrated. Lower polymerization

5   temperatures also gave better results (runs 3 and 4 in Table 1), but poor solubility of the polymerization products under these conditions prevented further pursuit of this approach. Polymerization carried out in THF at low temperature also did not give the desired result (run 5 in Table 1). Since one of the possible side reactions involves hydride elimination, with the formation of

10   stable lithium hydride (LiH) as the driving force, it is that using larger counterions such as potassium could minimize this process. This was indeed the case when benzylK, cumylK, or Naphthalene/K was used (Table 1, runs 6-8): the polydispersities were narrowed, but the molecular weights of these samples were always far lower than expected. Moreover, ^{1}H NMR data

15   revealed that the ratio of vinyl protons to nonvinyl protons is much lower than the theoretical value (1 /3). Side reactions other than chain transfer or termination must be involved in these polymerization procedures.

Polymerization of 1,3-CHD with Additives

       Additives play an important role in anionic polymerization. They have

20   been widely used to control the microstructures of polydienes and minimize side reactions in acrylate polymerization. Several monodentate additives, and the associated results are listed in Table 2. THF and sec-BuOLi, popular additives used to disrupt aggregation in anionic polymerization, failed to give positive results (runs 1 and 2 in Table 2). This suggests that chain aggregation

25   is not the main problem in the anionic polymerization of 1,3-CHD. The sec-BuLi/t-BuOK system, regarded as "second generation" super base, yielded polymers with reasonably narrow MWD (Table 2 run 3), but the molecular weights were much lower than anticipated. One possible reason is that the polymerization has to be carried out in THF at low temperature (-78°C), and

30   chains could not grow very long due to solubility problems (high MW PCHD has limited solubility in THF; the solubility also depends on the

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microstructure). Using *sec*-BuLi in THF/toluene (1/2 v/v) at -40°C, Zhang and Rubenstein selectively polymerized the styrene group in 4-(vinylphenyl)-1-butene to generate a polymer with a polystyrene backbone and functional butenyl side chains. See Zhang, H.; Ruckenstein, E. *Macromolecules* **1999**, *32*, 5495. However, their targeted molecular weight was only about 4000 g/mol. Not surprisingly, this system does not work well with 1,3-CHD (Table 2, run 4). Polydentate additives can change anionic polymerization processes dramatically due to their chelating effect. Natori and co-workers reported that the polymerization of 1,3-CHD using *n*-BuLi/TMEDA exhibits "living" character and that the ratio of *n*-BuLi and TMEDA that gives living character is crucial. See Natori, I. *Macromolecules* **1997**, *30*, 3696. It is believed that chain propagation and side reactions are strongly affected by the extent of the polarization of the Li-carbon bond in PCHDLi, and chelating by TMEDA offers the proper Li-C polarization. The *n*-BuLi/TMEDA initiation system is difficult to handle because the resulting polymers are difficult to dissolve in common solvents (Table 2, runs 5 and 6). Good results could only be achieved for low-MW targets. *n*-BuLi/PMDETA, similar to the *n*-BuLi/TMEDA initiation system, failed to produce materials with narrow poly-dispersities and predictable MWs (run 7 in Table 2). This is probably because PMDETA does not chelate as effectively as TMEDA, since the former is more bulky and has an extra chelating site. Bulkiness alone may not be the sole reason for effective chelating since DABCO, also bulky, is quite effective as discussed below. Other polydentate additives, such as DABCO, DPPE, and DME, used in combination with certain butyl-lithium isomers produced PCHD samples with relatively narrow MWDs and modest molecular weights as summarized in Table 2.

DME, a weak-chelating agent, can be used as an effective additive under carefully chosen conditions (Table 2, runs 10-12). The ratio of 1,4 to 1,2 addition in PCHD from this system is about 69/31. A group of PCHD samples having reasonably well-controlled molecular weights were made from *n*-BuLi/DME, and the results are listed in Table 3 (runs 8-16). One typical SEC

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trace of PCHD made using this initiating system is shown in Figure 2a. The polydispersities are quite narrow for low molecular weight samples, but at higher MWs narrow MWD materials are elusive, at least partially due to the poor solubility of the polymer. The three isomers of butyllithium in combination with DME or TMEDA yield striking differences in the polymerization processes. In contrast, the three butyllithium isomers in the presence of TMEDA give very similar results for the polymerization of styrene. With n-BuLi, the initiation process proceeds at the same rate as propagation, but with sec-BuLi and t-BuLi the initiation is faster than propagation. This alone should not cause the observed differences reported by Natori et al. in the polymerization of 1,3-CHD. Adequate data to allow elucidation of these differences were not presented. However, the very reactive species generated from $tert$-BuLi/TMEDA and sec-BuLi/TMEDA must undergo some detrimental reactions other than initiation and propagation. For DME, these differences are not surprising since DME has limited stability toward butyllithium. The protons in the β-positions are more acidic than that in TMEDA; thus, they are more readily abstracted followed by elimination. This process is fastest with $tert$-BuLi and slowest with n-BuLi. Lower temperatures also increase the stability of DME toward BuLi.

DPPE is also an effective additive. Some of the characteristics of PCHD obtained from BuLi isomers with DPPE are listed in Table 2 (runs 7-9). Better results could be achieved if the reactions were carried out under optimal conditions with regards to solvents, temperatures, and the amount of the additive (ratios of BuLi/DPPE). The 1,4 to 1,2 ratio of the PCHD from this polymerization system is about 57/43. DABCO, a bulky chelating agent, combined with sec-BuLi or $tert$-BuLi gives the best control over MW and polydispersity in the polymerizations of 1,3-CHD, as indicated in Table 2 (runs 13-15) and Table 3 (runs 1-7) (also Figure 2b). The resulting PCHD has a 1,4 to 1,2 additions ratio of 93/7. By chelating with DABCO, the C-Li bond in PCHDLi becomes strongly polarized, and consequently, chain propagations were facilitated while side reactions were minimized. The linearity of Mn with

conversion is often used as an experimental criterion to document that a polymerization is living. Unfortunately, this type of plot will only detect chain transfer reactions; it is not sensitive to chain termination. Natori used this plot to demonstrate that the n-BuLi/TMEDA/1,3-CHD system is living. To test whether there is any chain termination occurring during the polymerization process, 1,3-CHD was polymerized with n-BuLi/TMEDA or DME by sequential addition of the monomer. Figure 3 shows the SEC traces of PCHD obtained by this approach. After adding a second dose of monomer, the peak became significantly broader as shown in Figure 3b. This indicates that chain termination reactions do occur, with both DME and TMEDA. The large low molecular weight tail suggests that the chain transferred species could reinitiate 1,3-CHD.

Block Copolymerization Using BuLi without Additives

The successful control of the anionic polymerization of 1,3-CHD using certain initiating systems, as described above suggests the possibility of making well-defined PS-PCHD diblocks of high molecular weights and having a wide range of compositions. Several initiating systems and different polymerization sequences can be employed in this work. The conditions used and the characteristics of the resulting polymers are listed in Table 4. When styrene was polymerized by sec-BuLi in benzene followed by addition of 1,3-CHD without use of any additive, the PSLi initiated the polymerization of 1,3-CHD (Figure B (B)). The cross-propagation was accompanied by a color change from orange-red to yellow within 20 s. This simple procedure works well for making PS-PCHD block copolymers with short PCHD segments and thus low PCHD content in the copolymer. As shown in Figure 4a, the SEC trace of a PS-PCHD diblock copolymer (wt % of 1,3-CHD = 5.4) is symmetrical and monomodal. However, when the targeted 1,3-CHD composition in the PS-PCHD block copolymer was high (>20%), this polymerization was not well-controlled, as indicated by the low molecular weight shoulder in the SEC chromatogram (Figure 4c). These low MW byproducts arise from side reactions such as chain transfer and/or chain termination. Since 1,3-CHD can

undergo several detrimental reactions under anionic polymerization conditions (strong base) in addition to the desired propagation, the maximum attainable composition of PCHD in the copolymers with high molecular weight (>10 000 g/mol) is restricted regardless of the initial monomer ratio. The low molecular weight contaminants can be removed easily by solvent (toluene)/nonsolvent (methanol) fractionation. These results are similar to those reported by Zhong and Francois and Zhou et al. Zhong, X. F.; Francois, B. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 411; Francois, B.; Zhong, X. F. *Makromol. Chem.* **1990**, *191*, 2743; Francois, B.; Izzilllo, S.; Iratcabal, P. *Synth. Met.* **1999**, *102*, 1211; Zhou, J. Ph.D. Thesis, The University of Alabama at Birmingham, 1996. On the basis of infrared spectra, Zhong and Francois reported that the low molecular weight shoulder was pure PCHD. Consequently, they claimed that the metalated monomer formed by chain transfer reinitiated the polymerization of 1,3-CHD. Conversely, it has also been found that the fractionated low molecular weight material contains substantial amounts of PS, as revealed by the ^{1}H NMR spectra shown in Figure 5. The peak around 5.6 ppm is from the cyclohexene ring, and the peaks from 6.2 to 7.2 ppm are from styrene units. This is not surprising, since the initiation and chain propagation rates in the PSLi initiated 1,3-CHD polymerizations are not fast enough to avoid the side reactions that lead to chain terminations. In addition to chain termination by hydride abstraction (one of the well-known chain-transfer reactions for this monomer), 1,4-CHD, which is always present at some level in 1,3-CHD under strong base conditions, is a very effective chain terminator. While the possible reinitiation to create PCHD homopolymer quantitatively on the basis of the data at hand cannot be ruled out, the spectrum in Figure 5 strongly suggests that this process does not play a major role in our studies. These results show that it is very difficult to prepare PS-PCHD samples with high 1,3-CHD content by sequential polymerization of styrene, and then 1,3-CHD, using *sec*-BuLi alone as initiator. Table 4 also gives the characteristics of block copolymers prepared by polymerization of 1,3-CHD with *sec*-BuLi in benzene followed by the addition of styrene (Figure B (A)). PCHDLi chains can initiate

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the polymerization of styrene very rapidly under these conditions, as demonstrated by the yellow color turning to red-orange instantly upon addition of styrene. SEC traces for products of this reaction are shown in Figure 6. The polymerization of 1,3-CHD initiated by *sec*-BuLi in the absence of additives does not proceed in a controlled manner. The PCHD blocks are moderately polydisperse (Mw/Mn>1.2), as are the final PCHD-PS diblocks. With a short PCHD block, the resulting PCHD-PS block copolymer is monomodal (Figure 3a). However, bimodal PCHD-PS is formed when the PCHD block is longer (higher molecular weight) (Figure 3d). It is difficult to remove the low molecular weight shoulder from this material by conventional toluene/methanol fractionation. This is probably because part of the PCHDLi was deactivated before all the monomer (1,3-CHD) was consumed, and toluene is not a very good solvent for the PCHD block. More importantly, these results show that PCH-DLi can rapidly initiate the polymerization of styrene in hydrocarbon solvents even without the use of polar additives. This is in stark contrast to the copolymerization behavior of styrene and acyclic dienes.

When styrene and butadiene are simultaneously added to anionic initiators in hydrocarbon solvents, tapered block copolymer are formed because of the differences in reactivity ratios. Therefore, a "random" copolymerization behavior for styrene and 1,3-CHD can be anticipated. Francois et al. found similar behavior in *sec*-BuLi/cyclohexane initiation system. See Mr. Yunan Wan for his technical support. Francois, B.; Izzilllo, S.; Iratcabal, P. *Synth. Met.* **1999**, *102*, 1211. Therefore, *sec*-BuLi was used to polymerize styrene and 1,3-CHD simultaneously in benzene at room temperature. The composition of the polymerization products was monitored by ^{1}H NMR as a function of polymerization time, and the results are summarized in Figure 7. The monomodal character of the polymerization products as evidenced by SEC traces (Figure 8, solvent: THF) strongly suggests that they are not simple mixtures of PCHD and PS homopolymers. From Figure 7, one can see that the 1,3-CHD content in the polymerization products reached a rather high level quickly (30.5 mol % of 1,3-CHD in 20 min and 34.3 mol % in 120 min).

Under these reaction conditions, all the monomer was consumed in about 4 h. The composition does not change much after 120 min, and it is always slightly lower in 1,3-CHD content than anticipated on the basis of the monomer charge ratio. This is likely caused by the above-mentioned side reactions, which also

5   consume some 1,3-CHD. These findings suggest that the rate of reaction of PSLi with 1,3-CHD in benzene at room temperature is comparable to that of PCHDLi with styrene. Natori reported the copolymerization behavior of 1,3-CHD with styrene in cyclohexane using the n-BuLi/TMEDA (4/5) initiating system at 40°C. See Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 982. He

10   found that styrene was preferentially polymerized in the initial stage, and the polymerization of 1,3-CHD started only when most of the styrene was consumed. The higher reactivity of styrene in their study may be attributed to the presence of TMEDA, which can change the polymerization behavior dramatically because of its strong chelating effects with the growing chain

15   ends. Attempts to determine the sequence distribution in the copolymers by NMR were not successful because the spectra were very complex.

The MALDI-TOF-MS spectrum of the polymerization product from the first sampling of the "random copolymerization" is shown in Figure 9a along with a spectrum of a PS-PCHD diblock with similar composition (Figure 9b).

20   The single peak around 6000 g/mol and the monomodal SEC traces (Figure 9) suggest that the copolymerization was of a statistical nature. The drastic intensity differences in the two spectra are noteworthy. It was consistently observed that the MALDI-TOF-MS signals for PS-PCHD block copolymers are very weak. A possible reason for the low response of PS-PCHD block

25   copolymers in MALDI-TOF-MS spectra is that effective MALDI requires that individual polymer chain be dispersed in matrix crystals. PCHD segments are rather rigid and tend to aggregate during the preparation of MALDI samples. Consequently, only a small portion of the PS-PCHD chains can be ionized. However, the intensity for the "random copolymerization" product is much

30   higher than that for PS-PCHD diblock copolymers. This also implies that the styrene and 1,3-CHD units are statistically distributed in the former copolymer

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(i.e., not blocky), making aggregation of PCHD more difficult. Furthermore, the rates of crossover reactions from PCHDLi to styrene and vice versa were comparable for the *sec*-BuLi/benzene system based on visual observations (as noted above). Using the naphthalene/potassium initiation system in THF at -78°C, PCHD-PS-PCHD and PS-PCHD-PS triblock copolymers were successfully obtained with monomodal molecular weight distributions; however, the MWDs are rather broad (runs 10 and 11 in Table 4).

Block Copolymerization Using BuLi with Additives.

As discussed above, *sec*-BuLi alone does not polymerize 1,3-CHD in a controlled manner in hydrocarbon solvents. Therefore, it is difficult to synthesize PS-PCHD block copolymers with high molecular weights and covering a broad compositional range, as is necessary for morphological studies, using this approach. The use of certain additives can improve the situation. As shown in Table 4 (run 3), a small amount of THF can have a favorable impact on block copolymer formation via polymerization of 1,3-CHD followed by the addition of styrene. However, further attempts to target higher 1,3-CHD compositions and higher molecular weights were not successful because THF does not adequately suppress the side reactions. Moreover, THF may react with *sec*-BuLi at the polymerization temperature used. Natori reported that the *n*-BuLi/TMEDA initiating system could polymerize 1,3-CHD in a "living" manner. 1,3-CHD and styrene was sequentially polymerized using this initiator system; theses results are listed in Table 4 (runs 4 and 5) and Figure 10. When styrene was polymerized first, the SEC trace exhibited a tail at high molecular weight (Figure 10a). On the other hand, a low molecular weight shoulder was observed in the SEC chromatogram when 1,3-CHD was polymerized first (Figure 10b). The shoulder may arise from deactivated PCHDLi. In contrast to our findings, Natori reported that PCHDLi "living" chains could continue to grow by adding either styrene or 1,3-CHD. See Natori, I. *Macromolecules* **1997**, *30*, 3696; Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 982. However, tailing can be seen clearly in some of their published SEC chromatograms. A peak with extremely high molecular

weight (~1.3 million g/mol based on calibration with PS standards) was observed for many of the diblocks regardless of which monomer was polymerized first. Upon decreasing the solution concentration and repeating the SEC experiments, these peaks shifted to lower molecular weight (about 970

5   kg/mol calibrated with PS), and the fraction of the high molecular weight peak also decreased. When SEC experiments were run in $CHCl_3$, higher molecular weight peaks were also observed, but the positions moved to lower molecular weight (~500 kg/mol, based on calibration with PS). Variations of the molecular weight and the fraction of high and low molecular weight

10   components upon changing the polymer concentration or the SEC solvent suggest that micelles exist in solutions of some of these PS-PCHD block copolymers. As discussed, the n-BuLi/DME or sec-BuLi/DABCO initiating systems can polymerize 1,3-CHD in a controlled manner with regard to molecular weight and Mw/Mn. Thus, it is natural to try to extend those

15   approaches to the synthesis of PS-PCHD diblock copolymers. Typical results are listed in Table 4 (runs 9-12), and characterization data are given in Tables 5 and 6. Under these reaction conditions, PCHDLi efficiently initiates the polymerization of styrene and vice versa, as shown in Figure 11. When the targeted composition for PCHD was lower than 30 wt %, the resulting PS-

20   PCHD block copolymers were unimodal, and the polydispersities were low (Mw/Mn < 1.1). However, a shoulder corresponding to the first block was always seen in the SEC traces of the diblocks when the composition of PCHD was higher than 30 wt %. If styrene was polymerized first, this low molecular weight shoulder could be removed easily by solvent/nonsolvent fractionation

25   (toluene/methanol), and it mainly contained PS as revealed by ^{1}H NMR (Figure 12b). The compositions can be calculated from the intensities of styrene (6.2-7.2 ppm, 5H) and 1,3-CHD (5.4-5.8 ppm, 2H) repeating units. This is because 1,3-CHD terminated some PSLi and/or PS-PCHDLi chains. On the other hand, the low molecular weight shoulder was very difficult to remove by

30   toluene/methanol fractionation if 1,3-CHD was polymerized first. The shoulder was probably formed by the self-termination of the PCHDLi chains,

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since the possibility of PCHDLi chains being terminated by styrene is low. The difficulty in removing the low molecular weight component by toluene/methanol fractionation probably arises from the poor solubility of PCHD in toluene. The fractionation solution (supernatant) of a PS-PCHD

5   block copolymer (1,3-CHD polymerized first) contained a significant amount of PS (Figure 12a, peaks from 6.2 to 7.2 ppm), which indicates inefficient fractionation. However, the possibility of PS being formed by the polymerization of styrene initiated by the metalated 1,3-CHD species (the latter formed by chain transfer) cannot be excluded.

10 **Star Polymers**

The synthesis of the 3-arm PCHD homo-star polymers was performed according to Figure C. The key step of this synthetic route was the linking procedure. It was anticipated that the PCHDLi chain end, without end-capping with 1,3-BD, was sufficiently bulky that steric hindrance would prohibit its

15 complete reaction with the linking agent, CH_3SiCl_3. However, this reaction did yield three-arm star, although it required long reaction times (up to 2 weeks) as shown in Figure 13. The two-armed intermediate is clearly seen in the SEC trace of the first sampling. The possibility that some coupled material remains in the final product due to the limitations of SEC separation; however, the star

20 peak is quite symmetrical cannot be excluded. When the PCHDLi anions was capped with several 1,3-BD units, the chain ends became much less bulky and the linking reaction took place much faster, as shown in Figure 14. The linking reaction was so fast under the reaction conditions that the two-arm intermediate could not be detected after only 15 min of reaction. One possible reason for

25 this very rapid linking reaction is that the additive, DABCO, also functions as a promoter. To check this hypothesis, 1,3-BD was polymerized using sec-BuLi in benzene and linked the resulting anions with CH_3-SiCl_3 in the presence of DABCO. The condensation reaction proceeded quickly; no two-arm material was detected even at the first sampling (after 15 min of reaction), as shown in

30 Figure 15. Even though the linking reaction was allowed to continue, it was virtually finished in 1 h, as can be seen by comparing the SEC traces at 1 h and

1 day (Figure 3c,d). Tsiang found, consistent with these results, that the linking efficiency of (PB)₃SiCl with PS-PBLi was promoted from ~ 30% without a polar additive to >90% with a polar additive in 10 min. See Tsiang, R. C. C. *Macromolecules* 1994, *27*, 4399. The large arm peak was from the large excess of arm anions used in this experiment. The molecular characteristics of the resulting star polymers are summarized in Table 7. The measured molecular weights of the arms (weight-average molecular weight) are higher than those of the predicted (number-average molecular weight) probably because some initiators were killed by some impurities in the reactor. From Table 7 it can be seen that both arms and fractionated stars had very narrow molecular weight distributions (Mw/Mn < 1.1), indicating that the final star material is homogeneous.

Solvent (toluene)/nonsolvent (methanol) fractionation was used to remove the extra arm from the final three-armed PCHD star, and this proved to be difficult as shown in Figure 14E (also Figure 13D). This may arise from the modest molecular weights of the PCHD materials investigated. The polymer precipitate and solution phase separation of a polymer in the solvent/nonsolvent system depend on its molecular weight. The higher the molecular weight, the easier the phase separations and hence the higher the fractionation efficiency. However, there was one factor that prevented a pursuit of PCHD star homopolymers with higher molecular weight: polymers of 1,3-CHD are difficult to dissolve in common organic solvents if the molecular weight is high (>30 000 g/mol). A block-copolymer arm composed in part of polystyrene should improve the solubility.

The star-block copolymers were synthesized as shown in Figure D. Several star-block copolymers with both PS and PCHD as the outer blocks were synthesized, and the molecular characteristics of those polymers are summarized in Table 8. Molecular weights determined by light scattering and by MALDI-TOF-MS are in excellent agreement with one another if one considers that the former value is a weight-average and the latter a number-average molecular weight. Both SEC and the absolute methods confirm very

narrow molecular weight distributions for the star-block materials. The initial steps for these syntheses involved the preparation of living block copolymers that could be linked to make the desired star-block copolymers. For the arms with PS as the outer block, the polymerization of 1,3-CHD using the living polystyrene chain as initiator has proven to be feasible. It has been reported that the polymerization rate of 1,3-CHD initiated by PSLi is faster than that by BuLi. The progress of the synthesis for one $(PS-PCHD)_3SiCH_3$, as monitored by SEC, is shown in Figure 16. The monomodal nature of the PS block and PS-PCHD arm indicates their homogeneity. The small amount of coupled product seen in the chromatogram of the PS-PCHD arm is due to termination of the sample with methanol containing air. The linking reactions are very similar to these of PCHD three-arm star as discussed above. Excess arm can be removed by solvent/nonsolvent fractionation. However, if the targeted PCHD composition was too high, the monomer (1,3-CHD) was not consumed quickly. Over time, a small portion of 1,3-CHD molecules may isomerize to its 1,4-isomer, which can terminate some of the living chains (PS-b-PCHDLi). Such "dead polymer" can be removed easily by solvent/nonsolvent fractionation. The key to the synthesis of stars with PCHD as the outer block, $(PCHD-PS)_3SiCH_3$, is an efficient crossover reaction from PCHDLi to styrene. This reaction was previously demonstrated to be possible. It was also found that the sec-BuLi initiated polymerization of 1,3-CHD and styrene simultaneously resulted in random copolymers, which indicated the comparable cross reaction rate. Francois and co-workers also reported the quasi-alternate nature of the synchronized polymerization of styrene and 1,3-CHD using BuLi. See Francois, B.; Lartigau, C.; Da Cunha, L. *J. Chim. Phys.* 1998, *95*, 1226. Figure 17 shows the SEC chromatograms of one of the $(PCHD-PS)_3SiCH_3$ (run 5 in Table 8). The PCHD block shows a symmetric peak, but the PCHD-PS arm has a small peak at the low molecular weight end, which corresponds to the PCHD block as shown in Figure 17. There is no such problem when the molecular weight of the PCHD block is low (<10 000 g/mol). This indicates that the crossover reaction from PCHDLi to styrene is not 100% complete

when the PCHD block is very long. In this case, the 1,3-CHD polymerization takes longer to attain high molecular weight PCHD, and during this time some PCHDLi can be terminated or undergo chain transfer. These transferred species are not reactive enough to initiate styrene. Moreover, it is very difficult to remove this small peak by fractionation using toluene/methanol as the solvent/nonsolvent. This may be because toluene is not a good solvent for PCHD of high molecular weight. Under careful experimental condition, the unwanted lower molecular weight components can be fractionated away by using chloroform (as solvent) and hexane (nonsolvent). These results indicate that the PCHD chains are stiff. 46 Thus, these star-block copolymers are expected to have interesting morphological properties since they have both architectural asymmetries (star architecture) and conformational asymmetry (stiff chain).

Nanostructures

Applicants previously synthesized poly(styrene-block-cyclohexadiene) and collaborated on a study of the morphology of self-assembled, microphase-separated diblock copolymer of PS and PCHD. An unusual core-shell cylinder-in-cylinder morphology not previously found in neat diblock copolymers was observed in three different specimens of different molecular weights but all having similar composition (about 37% by volume PCHD). This structure consists of hexagonally packed cylinders of PCHD dispersed in a PS matrix; in the center of each PCHD cylinder there is a PS cylinder (Figure 18). This structure is the precursor to the novel nanotubes that are the subject of this proposal; by removing the PS inside and outside the PCHD cylinder, PCHD nanotubes may be produced.

The first synthesis of crosslinked polymer nanotubes from block copolymers was described by Guojun Liu in early 2000. See S. Stewart, G. Liu, "Block Copolymer Nanotubes", *Angew. Cherm. Int. Ed.*, *39*, 340 (2000). His group made these materials by ozone induced degradation of a polyisoprene phase within cylindrical micelles formed from an ABC triblock terpolymer. These nanotubes are acrylate based, and they will thus lack the

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high strength and thermal stability inherent in poly(phenylene) materials. Nevertheless, inspired by their elegant work, the present invention is directed to the core-shell cylinder-in-cylinder morphology that was observed for PS/PCHD diblocks as a means to synthesize functional polymer nanotubes.

5   To be able to remove the PS blocks it is necessary to have cleavable linkages connecting the two chain segments in the block copolymers. Such diblock copolymers can be synthesize by esterification of hydroxyl groups placed at one end of the PCHD chains with carboxylic acid groups placed at one end of the PS chains (see Figure E). The chemistries to be used for chain

10   end functionalization (carboxylation of PS chain ends with CO_2 and reaction of PCHD chain ends with ethylene oxide) are based on well-established literature procedures. For example, reaction of PCHD anions with ethylene oxide followed by protonation creates the desired end functionalized PCHD, while reaction of PS anions with CO_2 under appropriate conditions yields the

15   complementary end reactive PS. The compositions of the materials is controlled at about 37 vol % PCHD, since this is the composition that yielded cylinder-in-cylinder morphologies for three PS-PCHD diblocks, having different molecular weights. The diameter of the nanotubes is controlled by the molecular weight of the PCHD block.

20   Nanotubes are formed by casting films of the diblocks annealing and or using shearing to orient the dispersed cylinders, photocrosslinking of the PCHD phase, hydrolysis of the ester linkages under acidic conditions, and washing out of the PS material with solvents. The processing conditions controls the extent of long range order present in the microphase separated

25   structure and can be used to control the aspect ratio – and thus properties – of the nanotubes. THF or dioxane containing aqueous acid may be used for hydrolysis. This solvent system will swell the polymer phases permitting cleavage of ester linkages to occur. The removal of the PS phase, especially the PS inside the PCHD nanocylinders, requires careful solvent selection to

30   preferentially swell the crosslinked PCHD domains. It will also be possible to carry out a partial hydrolysis in such a manner as to create a "nanotube brush"

(nanotubes projecting out from a surface in the z direction). PCHD can be aromatized using p-chloranil or the more efficient reagent 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. These nanotubes have hydroxyl groups on their surface due to cleavage of the ester linkages. These groups are then used to attach things to the nanotubes or to promote interactions between the nanotubes and some matrix in which they are dispersed. These surfaces are above be chemically modified to create a wide range of tunable surface chemistries.

Applicants note some difficulty in removing all the PS from the interior of the PCHD tubes. However, if this problem is encountered, one option is to aromatize the PCHD and then remove the PS by pyrolysis (polyphenylene is extremely thermally stable). This strategy was previously used to create a non-equilibrium "honeycomb morphology" from a PS/PP block copolymer. It is also possible that the aromatization reaction will not occur throughout the PCHD phase but only near the surface. This may prove to impart adequate properties to the nanotubes. However, it is also possible that thermal treatment (pyrolysis) of these tubes, similar to the manner by which poly(acrylonitrile) in converted to conventional carbon fibers, might yield unique and useful nanotubes.

Nanotubes based on this block copolymer precursor approach are intermediate in diameter to single-walled carbon nanotubes and lipid tubules, with diameters ranging from about 10-100 nm and controlled through block copolymer molecular weight (MW), composition, and optional addition of homopolymer. Their lengths can be controlled over the range of tens to many thousands of nm, giving them controllable and potentially very long aspect ratios. Compared to other nanotubes, these materials are inexpensive to manufacture, amenable to scale up, and ordered arrays on a surface may be readily created through self-assembly. In addition, the synthesis route will yield products with controlled surface functionality. Both conducting and non-conducting materials can be generated. In addition to the synthesis of nanotubes, the general synthetic approach described herein could also be used

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to synthesize PP nanocylinders (nanowires after doping), nanospheres (a new type of quantum dot), or sheets of nanoscale thickness.

Other morphologies (spheres, cylinders, or lamellae of PCHD) could also be obtained appropriate choice of composition of PS/PCHD block copolymers. Morphological characterization is a key step in any effort to relate nanoscale structure to properties. The core-shell PS-PCHD block copolymers and the nanotubes produced from them are characterized via transmission electron microscopy (TEM), field emission gun scanning electron microscopy (FEGSEM), and small angle scattering experiments. For observation of the PS-PCHD diblock core shell morphology prior to hydrolysis and nanotube formation, Cryoultramicrotoming will be used to produce ultra thin sections approximately 300-800 Å thick. Staining with OsO_4 allows TEM imaging of the nanoscopic PCHD hollow tubes, which have self assembled onto a hexagonal lattice (34). Small angle scattering experiments are performed in order to accurately determine the lattice symmetries and dimensions of the morphologies. Control of nanotube size via control of molecule weight and composition will be confirmed by microscopy and scattering; it is important to employ a combination of both TEM and scattering techniques in the determination of morphological structure since the two techniques compensate for each others weaknesses. SAXS (X-ray) can be done using a rotating anode sources and a two-dimensional area detector at the University of Massachusetts.

After hydrolysis and nanotube formation, the dispersed nanotubes are deposited on amorphous carbon substrates for imaging via TEM and electron diffraction characterization of crystallinity in cases where the structures are converted to PP. The nanotubes are then imaged via FEGSEM which is capable of resolving structures of 4 nm without need of metal coatings. In cases where the tubes are doped to provide enhance electrical conductivity, characteristic X-ray detectors on both the TEM and FEGSEM instruments will allow spatially resolved mapping of elemental composition variations. Atomic force microscopy will also be used to observe the nanotubes. AFM provides a

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convenient means of accurately measuring tube dimensions, and mechanical properties of individual tubes can be probed by applying pressure with the AFM tip.

5   The proposed structures have a number of exciting optical device applications as well as uses as nanoprobes and in field emission. Ordered two-dimensional arrays of the nanotubes may be made by solvent etching of a surface having the cylinders oriented perpendicular to the surface. Nanolithographic patterning may be performed by selective masking during the UV irradiation step. The ordered tubes can be selectively filled with desired 10   materials, e.g. metals. Other architectures besides tubes (nano-cylinders, -plates) can also be made based on cylindrical or lamellar morphologies. These molecular objects can be useful for miniaturization of optical and electrical devices and micromechanical systems (MEMS). Surface initiated polymerization (SIP) can be utilized to grow PCHD polymer, patterned or non-15   patterned, on surfaces. By combining microcontact printing and dip-pen nanolithography with SIP, PCHD precursor polymer brushes can be grown as arrays and subsequently aromatize these structures. These materials will exhibit interesting electrical and optical properties that can potentially benefit the display and semiconductor industries.

20   Numerous studies could be performed with scanning probe microscopy. These range from high-resolution morphological characterization of the nanotubes themselves to more exotic measurements including attaching or growing a nanotube on the tip of a cantilever. This will enable experiments the user can functionalize the apex of the nanotube with a specific molecular 25   species and probe a companion surface to measure molecule-molecule interactions. An AFM tip with a nanotube attached has also been shown to enhance resolution for imaging molecules on surfaces. Other applications include growing the nanotubes between the apex of two cantilever tips and measuring the mechanical properties of the nanotubes.

30   This application foresees the ability to grow a nanotube that is itself piezoelectric in nature. There have been some recent developments in

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piezoelectric copolymers, but these have been bulk materials. It would be very significant if one can produce a PP nanotube that produces piezoelectric voltage when bent or can be induced to move in specific ways when a voltage is applied. Nanomachines and nanoelectronic devices would evolve quickly

5   from such structures.

Experimental Procedures

PCHD Synthesis

Materials. Benzene (Fisher, >99%), cyclohexane (Fisher, >99%), THF (Aldrich, 99.9%), and methylcyclohexane (Aldrich, 99%) were purified

10   according to the anionic polymerization standards, as described in the literature.   TMEDA   (Aldrich,   >99%),   N,N,N',N',N'-pentamethyldiethylenetriamine (PMETE-DA, Aldrich, 99%), DME (Acros, >99%), and 1,2-dipiperidino-ethane (DPPE, Sigma, >99%) were stirred over freshly crushed CaH_2 powder for at least 24 h and distilled from potassium (K)

15   mirror twice and finally from potassium/sodium alloy under high vacuum. Naphthalene (Aldrich, >99%) and 1,4-diazabicyclo[2.2.2]octane (DABCO, Aldrich, 98%) were sub-limed under high vacuum three times and then diluted in cyclohexane and benzene, respectively. Potassium *tert*-butoxide (*t*-BuOK, Aldrich, 95%) was diluted in THF, and phenyllithium (PhLi, Aldrich, 1.8 M in

20   ether and cyclohexane) and *tert*-butyllithium (*t*-BuLi, Aldrich, 1.5 M in pentane) were used as received. 1,3-CHD (Aldrich, 97%) was cleaned by treating over CaH_2 followed by exposure to sodium mirrors at room temperature 2-3 times for 24 h each. This "roughly" purified 1,3-CHD was finally treated with n-BuLi or dibutylmagnesium (MgBu2 Aldrich, 1.0 M in

25   heptane) at 0°C for 30 min just before the polymerization. Butyllithiums (sec-BuLi and n-BuLi) were prepared by reactions of the corresponding butyl chloride with lithium powder in hexane under vacuum. Cumyl potassium (CumylK) and benzyl potassium (BenzylK) were made via published methods.

Polymerization and Characterization.   All polymerizations were

30   performed under high vacuum using custom-made glass reactors. Break-seals allowed introduction of reagents sequentially, and constriction seal-offs

permitted intermittent removal of products. The molar ratio of additive to initiator was from 1.5 to 3 unless otherwise stated. In a typical polymerization experiment, about 75 mL of pure benzene was distilled into a reactor with all the purified reagents attached via break-seals. The reactor was removed from the vacuum line after evacuation. Then about 4.3 mL of *sec*-BuLi (in hexane, 7 x 10^{-5} mol/mL) and 3.5 mL of DABCO (in benzene, 2.1 x 10^{-3} mol/mL) were introduced into the reactor. After stirring for 5 min at room temperature, 4.4 g (0.055 mol) of 1,3-CHD was added. The reaction was allowed to continue for about 6 h and terminated with degassed methanol. The polymer solutions were precipitated in a large excess of methanol with 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) added to prevented oxidative degradation. The stabilized polymer was isolated by filtration and dried under high vacuum. Number-average molecular weights (Mn) and polydispersity indices (Mw/Mn, where Mw is weight-average molecular weight) were obtained from size exclusion chromatography (SEC) relative to calibration with polystyrene (PS) standards in either THF or chloroform ($CHCl_3$). SEC in THF (flow rate: 1 mL/min; Waters Styragel 100, 500, 10^3,10^4, and 10^5 Å columns) was obtained using a Waters 510 pump equipped with a Waters 410 differential refractometer detector; SEC in $CHCl_3$ (flow rate: 0.3 mL/min; columns: Polymer Lab. PL-Gel 5 *i*m MiniMIX narrow bore columns with pore size from 100 to 10^5 Å) was acquired from a Waters 2690 system with a Waters 2410 refractive index and a Waters 996 photodiode array detectors. Proton nuclear magnetic resonance (^{1}H NMR) experiments were carried out in $CDCl_3$ at 30°C using a Bruker ARX-300 instrument. The 1,2 to 1,4 ratios were determined from the relative areas of protons that are adjacent to the double bond (α position) and those in β positions. Each 1,2-unit has three α protons and three β protons, while a 1,4-unit has two α protons and four β protons. The Mn of the product of the polymerization described above is 20.1 kg/mol with a polydispersity of 1.04, as determined by SEC in THF.

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Block Co-polymers

Materials. All materials were purified to anionic polymerization standards, as reported in the literature, and brief procedures are described as follows. Benzene (Fisher, >99%) and hexanes (Fisher, $\geq$ 99.9%) were purified by stirring over concentrated sulfuric acid for 2 weeks, followed by drying over ground calcium hydride (CaH_2) on the vacuum line overnight. After degassing several times, these solvents were distilled into calibrated cylinders containing n-BuLi (Aldrich, 1.6 M in hexanes) and a few drops of styrene. The persistence of the bright orange color (polystyryllithium, PSLi) indicated the purity of the solvents. Tetrahydrofuran (THF, Aldrich, 99.9%) was refluxed over sodium for at least 6 h and collected into a flask containing sodium dispersion under argon. This flask was then connected to the vacuum line; the solvent was degassed and distilled into a flask with sodium/potassium alloy. After stirring for some time, the bright blue color that developed showed that the THF was free from impurities deleterious to anionic polymerizations. TMEDA (Aldrich, >99%) and DME (Acros, >99%) were purified using the same procedures as for THF except potassium (K, Aldrich, 98%) mirrors were used instead of sodium dispersion. Styrene (Aldrich, 99%) was dried over CaH_2 and finally distilled from dibutylmagnesium (Mg-Bu$_2$, Aldrich, 1.0 M in heptane) and collected in ampules using a short-path distillation apparatus. 1,4-Diazabicyclo[2.2.2]-octane (DABCO, Aldrich, 98%) was purified by sublimation three times under vacuum and then diluted in benzene or cyclohexane. Naphthalene was also purified by sublimation three times but diluted in THF. 1,3-CHD (Aldrich, 97%) was cleaned by treating over CaH_2, sodium mirror (3 times), and finally n-BuLi or MgBu$_2$. Butyllithium (*sec*-BuLi or n-BuLi) was prepared from the reaction of 2-chlorobutane (Aldrich, g 99%) or 1-chlorobutane (Aldrich, $\geq$ 99%) with lithium powder (Aldrich, high sodium, 99%) in hexane. Potassium naphthalenide was made by reacting naphthalene with a K mirror in THF at -78°C for 2 h just before polymerization.

Polymerization. All polymerizations were carried out under high vacuum using custom-made glass reactors, and detailed procedures are outlined in the literature. It is possible to synthesize PS-PCHD diblocks by either polymerizing 1,3-CHD first, followed by addition of styrene (Figure B, (A)), or

5   by polymerizing styrene first, followed by addition of 1,3-CHD (Figure B, (B)). Both approaches were employed in this work. In a typical experiment to prepare PS-PCHD diblock copolymer, about 85 mL of purified benzene was distilled into an evacuated reactor with attached ampules containing all the necessary purified reagents. The reactor was removed from the vacuum line by

10   heat-sealing after degassing. A 5.5 mL aliquot of sec-BuLi (9.7×10^{-5} mol/mL in hexanes) was added to the solution followed by 2.3 g (0.022 mol) of styrene. The polymerization started right away (deep red color) and was allowed to continue for 6 h before taking an aliquot (~ 1 mL) for characterization. Size exclusion chromatography (SEC) and matrix-assisted laser

15   desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) results indicated the molecular weight of the first block was 4.52 kg/mol with a polydispersity of 1.08. About 2.5 mL of DABCO (3.2×10^{-4} mol/mL in benzene) was introduced into the reactor through a break-seal. After stirring about 5 min at room temperature, 6.4 g (0.08 mol) of 1,3-CHD was then added

20   from another ampule. The solution turned to golden yellow quickly and was allowed to continue to polymerize for another 6 h before terminating the reaction with degassed methanol. The final product was found to have a weight-average molecular weight (Mw) of 18.6 kg/mol (from multiangle laser light scattering (MALLS)), a number-average molecular weight (Mn) of 15.4

25   kg/mol (from MALDI-TOF-MS), a polydispersity (Mw/Mn) of 1.03, and a composition of PCHD with 66.0 wt % (from ^{1}H NMR). For a representative PCHD-PS diblock copolymer, about 90 mL of benzene was used as solvent. After stirring of 3.1 mL of sec-BuLi (9.7×10^{-5} mol/mL in hexanes) with 1.6 mL of DABCO (3.2×10^{-4} mol/mL in benzene) for 5 min at room temperature,

30   3.0 g (0.038 mol) of 1,3-CHD was added and the polymerization was continued for 6 h. A small aliquot (~1 mL) was taken to characterize the PCHD block

before adding 4.4 g (0.042 mol) of styrene and allowing it to polymerize for another 6 h. The first block was found to have Mn of 11.7 kg/mol (MALDI-TOF-MS) with Mw/Mn = 1.11. The polymerization was stopped by adding degassed methanol. The final diblock copolymer had Mw of 41.8 kg/mol

5   (MALLS), Mn of 44.2 kg/mol (SEC), Mw/Mn of 1.07 (SEC), and a composition of PCHD of 39.4 wt % (from ^{1}H NMR). The polymer solutions were precipitated in a large excess of methanol with 2,6-di-tert-butyl-4-methylphenol (butylated hydroxytoluene, BHT) added as antioxidant. The final polymer was isolated by filtering and drying under high vacuum. For

10   some samples, solvent/nonsolvent fractionation (toluene/methanol) was used to remove homopolymer contaminants. Methanol was added slowly to the polymer solution in toluene (concentration ~ 0.5% w/v) until turbidity appeared. The solution was then heated gently while stirring to eliminate turbidity, and it was then transferred to a warm separatory funnel. This system

15   was kept undisturbed overnight to allow phase separation. This procedure was usually repeated until SEC could detect no undesirable products.

Characterization. SEC experiments in THF were carried out at 30°C using a Waters 510 pump and Waters 410 differential refractometer detector (flow rate: 1 mL/min; columns: Waters 100, 500, 10^3, 10^4, and 10^5 Å). SEC

20   experiments in chloroform (CHCl$_3$, flow rate: 0.3 mL/min) were done at 30°C on a Waters 2690 system with Waters 2410 refractive index and Waters 996 photodiode detectors. Two Polymer Laboratories 5 μm PL-gel MiniMIX narrow bore columns with pore size from 100 to 10^5 Å were used. This system was also connected to a Wyatt DAWN DSP MALLS detectors equipped with 5

25   mW linearly polarized He-Ne laser (wavelength) 632.8 nm). The MALLS unit has 18 detectors with fixed detector angles from 22° to 147°. To calculate the absolute molecular weight, dn/dc values of the samples are required. The refractive index increments (dn/dc) for PCHD and PS in CHCl3 were measured with a Brice-Phoenix differential refractometer, operating at 632.8 nm and

30   calibrated with aqueous potassium chloride solutions. ^{1}H NMR experiment was carried out in CDCl3 at 30°C using a Bruker ARX 300 instrument.

MALDI-TOF-MS spectra were obtained with a PerSeptive Biosystems Voyager Elite DE instrument using linear mode. A 20 kV acceleration was used with delayed extraction. The spectra were collected by summing 250 shots by using a nitrogen laser (337 nm, 3 ns pulse width) operated at 5 Hz. Samples were prepared by mixing matrix (dithranol, ~ 10 mg/ mL) and ionizing salt (silver trifluoroacetate, ~ 1 mg/mL) with polymer species (~ 1 mg/mL) in a ratio of 20/20/1 (v/v). $CHCl_3$ was the solvent. Approximately 0.5 μL of the sample solution was applied to the sample plate. All spectra were baseline corrected and smoothed. Peptide standards were used to calibrate the instrument externally.

Star Polymers

Materials. All materials were purified to anionic polymerization standards as reported in the literature, and brief procedures were described as follows. Benzene (Fisher, >99%) and hexanes (Fisher, $\geq$ 99.9%) were purified by stirring over concentrated sulfuric acid for 2 weeks followed by drying over grounded calcium hydride (CaH_2) in a vacuum line overnight. After degassing several times, they were distilled into calibrated cylinders containing n-BuLi (Aldrich, 1.6 M in hexanes) and a few drops of styrene. The persistence of the bright orange color (polystyryllithium) indicated the purity of the solvents. Tetrahydrofuran (THF, Aldrich, 99.9%) was refluxed over sodium for at least 6 h and collected into a round flask containing sodium dispersions under argon. This flask was then connected to the vacuum line; the solvent was degassed and distilled into a flask with sodium/potassium alloy. After stirring for some time, the bright blue color showed that the THF was free from impurities deleterious to anionic polymerizations. 1,3-Butadiene (1,3-BD, Aldrich, $\geq$ 99%) was condensed in a flask containing freshly grounded CaH2 at -78°C and connected to high-vacuum line. After stirring at -10°C for 2 h, the monomer was distilled into another flask containing sodium chunks and stirred for 30 min at -10°C. The monomer was then exposed to n-BuLi for 30 min at -10°C, collecting the desired amount into calibrated ampules, and diluted with purified hexanes. Styrene (Aldrich, 99%) was dried over CaH_2 and finally distilled

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from dibutylmagnesium (MgBu2) and collected in ampules using short-path distillation apparatus. 1,4-Diazabicyclo[2.2.2]octane (DABCO, Aldrich, 98%) was purified by sublimation three times under vacuum and then diluted in benzene or cyclohexane. 1,3-CHD (Aldrich, 97%) was cleaned by treating over CaH2, sodium mirror (three times), and finally n-BuLi or MgBu2, and the details was described elsewhere. 28 sec-Butyllithium (sec-BuLi), prepared from the reaction of sec-butyl chloride (Aldrich, ≥ 99%) with lithium powder in hexane, was used as the initiator. Methyltrichloro-silane (CH3SiCl3, United Chemical Technologies, Inc., ≥ 99.9%) was stirred over CaH2 overnight, followed by fractional distillation on the vacuum line (collecting the middle 1/3 fraction) and then subdivided into ampules. It was diluted to the desired concentration with purified hexane.

Polymerization. All polymerizations were carried out under high vacuum using custom-made glass reactors with sec-BuLi/DABCO (1/2) as the initiating system and benzene as the solvent. Detailed procedures are outlined in the literature. PCHD-PS and PS-PCHD arms were made by sequential addition of monomers. Following the completion of each polymerization stage, an aliquot was taken for characterization. In a typical experiment, about 90 mL of purified benzene was distilled into a high-vacuum evacuated reactor with attached ampules containing all the necessary purified reagents. The reactor was removed from the vacuum line after degassing. Then 3.8 mL of sec-BuLi (1.23 x 10⁻⁴ mol/mL in hexanes) and 2.5 mL of DABCO (2.8 x 10⁻⁴ mol/mL in benzene) in ampules were introduced into the reactor through break-seals. After stirring about 5 min at room temperature, 4.6 g (0.058 mol) of 1,3-CHD was added. The polymerization started right away (golden yellow color) and was allowed to continue for about 6 h. An aliquot (~1 mL) was taken, and SEC results indicated the MW of the arm was 13.6 kg/mol (calibrated with polystyrene standard) with MWD) 1.05. After end-capping the PCHD living chains with about 0.2 mL of butadiene, the linking reaction started by adding 2.9 mL of CH3SiCl3 (4.6 x 10.5 mol/mL in hexanes). The linking process was monitored by taking aliquots on a scheduled basis and checking with SEC.

After the linking reaction was completed, degassed methanol was added to terminate the excess arm. The polymer solutions were precipitated in a large excess of methanol with 2,6-di-tert-butyl-4-methylphenol (butylated hydroxytoluene, BHT) added. The final polymer was filtered and dried under high vacuum. After fractionation, the Mw of the three-arm PCHD star from the polymerization described above is 41.2 kg/mol with a MWD of 1.06 as determined by SEC equipped with a multiangle laser light scattering (MALLS) detector.

Solvent/nonsolvent (toluene/methanol) fractionation was used at room temperature to remove the excess unreacted arm material. Methanol was added slowly to the polymer solution in toluene (concentration ~ 0.5% w/v) until turbidity appeared. The solution was heated gently to eliminate turbidity while stirring. It was then transferred to a warm separatory funnel. This system was left undisturbed overnight to allow phase separation. This procedure was repeated as necessary.

Characterization. SEC experiments in THF were carried out at 30°C using a Waters 510 pump and Waters 410 differential refractometer detector (flow rate: 1 mL/min; columns: Waters 100, 500, 10^3, 10^4, and 10^5 Å). SEC experiments in chloroform ($CHCl_3$, flow rate 0.3 mL/min) were done at 30°C on a Waters 2690 system with Waters 2410 refractive index and Waters 996 photodiode detectors. Two Polymer Laboratories 5 μm PL-gel MiniMIX narrow bore columns with pore size from 100 to 10^5 Å were used. This system was also connected to a Wyatt DAWN DSP MALLS detectors equipped with 5 mW linearly polarized He-Ne laser (wavelength) 632.8 nm). The MALLS unit has 18 detectors with fixed detector angles from 22° to 147°. To calculate the absolute MW, dn/dc values of the samples are required. The refractive index increments (dn/dc) for PCHD and PS in $CHCl_3$ were measured with a Brice-Phoenix differential refractometer, operating at 632.8 nm and calibrated with aqueous potassium chloride solutions (dn/dcPS) 0.172 mL/g and dn/dcPCHD) 0.125 mL/g). The dn/dc for the star-block polymers were calculated from the weighted average dn/dcstar) xPS(dn/dc)PS + (1 - xPS)(dn/dc)PCHD, where

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xPS is the PS weight fractions determined by ^{1}H NMR. The ^{1}H NMR experiment was carried out in CDCl$_3$ at 30°C using a Bruker ARX 300 instrument. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were obtained with a PerSeptive Biosystems Voyager Elite DE instrument using linear mode. 20 kV acceleration was used with delayed extraction. The spectra were collected by summing 250 shots by using a nitrogen laser (337 nm, 3 ns pulse width) operated at 5 Hz. Samples were prepared by mixing matrix (dithranol, ~ 10 mg/mL) and ionizing salt (silver trifluoroacetate, _ 1 mg/mL) with polymer species (~1 g/mL) in a ratio of 20/20/1 (v/v). CHCl3 was the solvent. Approximately 0.5 μL of the sample solution was applied to the sample plate. All spectra were baseline corrected and smoothed. Peptide standards were used to calibrate the instrument externally.

Any patents or publications mentioned in this specification are indicative of the level of those skilled in the art to which the invention pertains. These patents and publications are herein incorporated by reference to the same extent as if each individual publication was specifically and individually indicated to be incorporated by reference.

The present examples along with the methods, procedures, treatments, molecules, and specific compounds described herein are presently representative of preferred embodiments, are exemplary, and are not intended as limitations on the scope of the invention.

While the foregoing description was directed to the preparation of some particular materials, it will be understood that in view of the teaching presented herein, one of skill in the art could readily prepare a variety of modified viral materials, all of which are within the scope of the present invention.

We claim:

Table 1 Polymerization of 1,3-CHD Using Various Anionic Initiators (without additives)

Run	Initiator	Solvent/Temp (°C)	[CHD] mole/L	[I] %10³ mole/L	Yield %	$M_{n,Cal}$ %10⁻³	$M_{n,SEC}$ %10⁻³	M_w/M_n (SEC)
1	s-BuLi	Benzene/20	0.53	1.40	53	29.9	7.6	2.17
2	s-BuLi	Benzene/20	0.59	4.69	59	9.9	7.3	1.49
3	s-BuLi	Ben./Hex./0 [a]	1.04	5.56	68	15.0	13.1	1.22
4	s-BuLi	MeCyclohex./-70 [b]	0.88	3.51	83	20.0	18.8	1.43
5	s-BuLi	THF/-78	1.00	7.36	47	10.9	5.1	4.92
6	BenzylK	THF/-78	1.45	2.63	93	44.1	26.0	1.38
7	CumylK	THF/-78	1.29	5.75	89	17.9	15.1	1.30
8	Naphthalene/K	THF/-78	1.09	6.99	98	25.0	17.4	1.40
9	t-BuLi	Benzene/20	1.05	3.65	75	5.8	9.5	2.07
10	t-BuLi	Benzene /20	1.14	9.96	49	9.1	7.1	1.77
11	PhLi	Benzene/20	1.05	3.04	71	27.6	10.6	2.06

Table 2 Polymerization of 1,3-CHD using BuLi with Additives

Run	Initiator	Solvent/Temp (°C)	Additive	[Add.]/[I]	[CHD] mole/L	[I] %10³ mole/L	Yield %	$M_{n,Cal}$ %10⁻³	$M_{n\ SEC}$ %10⁻³	M_w/M_n (SEC)
			Mono-dentate Additive							
1	s-BuLi	Benzene/0	THF	19.2	1.02	8.16	37	10.0	2.2	4.28
2	s-BuLi	Benzene/20	s-BuOLi	1.5	0.82	2.20	78	30.1	4.97	2.21
3	s-BuLi	THF/-78	t-BuOK	2.9	1.18	4.86	57	19.4	3.6	1.19
4	s-BuLi	Toluene/-40 [a]	THF		0.97	5.55	23	13.9	3.6	1.77
			Poly-dentate Additive							
5	n-BuLi	Cyclohexane/40	TMEDA [b]	1.21	0.70	5.99	100	9.3	18.4	1.38
6	n-BuLi	Cyclohexane/40	PMDETA [b]	1.27	0.81	2.62	100	24.6	27.9	1.61
7	n-BuLi	Benzene/20	DPPE [b]	2.33	1.05	8.35	100	10.1	5.1	1.07
8	s-BuLi	Benzene/20	DPPE	3.02	1.14	7.80	92	11.7	NOT Soluble	NOT Soluble
9	t-BuLi	Benzene/20	DPPE	3.09	1.04	7.65	88	10.9	NOT Soluble	NOT Soluble
10	n-BuLi	Benzene/0	DME [b]	4.43	0.58	6.00	98	7.7	11.3	1.07
11	s-BuLi	Benzene/20	DME	4.80	1.09	3.38	16	25.9	6.3	4.73
12	t-BuLi	Benzene/20	DME	4.71	1.75	6.80	9	20.6	4.9	3.18
13	n-BuLi	Benzene/20	DABCO [b]	3.19	0.90	5.08	94	14.2	37.8	1.24
14	s-BuLi	Benzene/20	DABCO	2.47	0.79	4.29	100	14.6	20.1	1.04
15	t-BuLi	Benzene/20	DABCO	1.54	1.15	5.18	87	17.8	17.6	1.11

Table 3 Poly(1,3-Cyclohexadiene) Homopolymers from BuLi and DABCO or DME

Run	[Additive]/[I]	[CHD](mole/L)	[I]%10^{-3} (mole/L)	$M_{n,Cal}\%10^{-3}$	$M_{n,SEC}\%10^{-3}$	M_w/M_n (SEC)
			s-BuLi/DABCO/Benzene / 20°C			
1	1.4	1.68	35.11	3.8	4.4	1.06
2	1.7	1.20	12.63	7.6	9.1	1.05
3	1.8	1.13	9.52	10.5	13.8	1.03
4	2.5	0.79	4.29	14.7	20.1	1.04
5	2.0	0.82	2.84	23.1	27.8	1.12
6	2.3	1.14	3.10	29.5	36.0	1.31
7	2.1	1.21	2.10	46.3	42.9	1.34
			n-BuLi/DME/Benzene/0°C			
8	1.7	1.04	17.6	4.7	4.0	1.13
9	2.39	0.69	6.0	7.1	11.3	1.07
10	1.45	1.05	12.2	9.5	13.8	1.12
11	1.65	1.63	8.91	13.7	17.9	1.21
12	2.09	0.77	2.87	16.3	21.1	1.19
13	1.75	1.75	7.35	19.0	28.2	1.24
14	2.15	1.18	3.28	28.7	36.5	1.51
15	1.74	1.77	3.60	39.4	42.9	1.43
16	4.89	0.95	1.51	50.2	Not soluble	

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Table 4   Characteristics of PS-PCHD Block Copolymer form BuLi with Various Additives

Run	Additive	[Add]/[I]	[ST] mole/L	[CHD] mole/L	[I] %10^3 mole/L	M$_n$^{a} %10^{-3}	Mw/Mn^a	Comp.^{b} wt% PCHD	Remarks
1^c	No additive		0.449	0.646	2.78	22.7	1.22	38.4	St first
2^c	No additive		0.321	0.777	15.4	8.0	1.25	70.7	CHD first
3^c	THF	16.8	0.294	0.266	4.13	15.8	1.15	43.7	St first
4^d	TMEDA	1.25	0.551	1.083	3.52	Multi-modal			CHD first
5^e	TMEDA	1.27	0.637	0.625	3.47	23.7	1.09	45.1	St first
6^e	TMEDA	1.33	0.803	1.015	8.53	bimodal			CHD first
7	Naphth./K/THF/-78°C		0.737	0.620	11.15	19.3	1.25		St first
8	Naphth./K/THF/-78°C		0.656	0.959	8.01	23.4	1.41		CHD first
9^f	DME	5.71	0.240	1.354	7.01	27.0	1.04	82.2	St first
10^f	DME	5.60	0.321	0.900	5.52	33.2	1.07	81.5	CHD first
11^g	DABCO	1.74	0.719	0.539	4.88	6.21	1.06	34.7	St first
12^g	DABCO	1.63	0.564	0.501	5.47	44.2	1.07	39.4	CHD first

a: From SEC in THF; b: From ^{1}H-NMR; c: s-BuLi in THF; d: s-BuLi in benzene at room temperature; e: n-BuLi in benzene at room temperature; f: n-BuLi in Cyclohexane at 40°C; g: s-BuLi in Benzene at room temperature.

e: n-BuLi in Benzene at 5°C; f: n-BuLi in Benzene at room temperature.

Table 5 Characteristics of PS-PCHD Diblock Copolymers from s-BuLi/DABCO/Benzene/20°C

Run	[ST] mole/L	[CHD] mole/L	[I] $\%10^3$ mole/L	M_n^a $\%10^{-3}$	M_w/M_n [a]	M_w^b $\%10^{-3}$	M_n^c $\%10^{-3}$	Comp.[d] wt% PCHD
1	0.673	0.542	8.33	15.3	1.03	19.3	17.0	38.2
2	0.492	0.340	4.02	26.7	1.06	32.9	28.4	52.7
3	0.719	0.539	4.88	22.9	1.03	26.1	23.8	34.7
4	1.05	1.23	7.00	16.9	1.03	18.6	15.4	66.0
5	1.07	0.225	7.38	15.7	1.04	17.7	16.5	11.4
6	0.175	1.64	10.64	17.1	1.04	21.9	19.1	85.1

[a]: From SEC; [b]: from SEC-MALLS; [c]: from MALDI-TOF-MS; [d]: via ^{1}H-NMR in CDCl$_3$

Table 6   Characteristics of PS-PCHD Diblock Copolymer from n-BuLi/DME/Benzene/5°C

Run	[ST] mole/L	[CHD] mole/L	[I] $\%10^3$ mole/L	M_n [a] $\%10^{-3}$	Mw/Mn [a]	M_w [b] $\%10^{-3}$	M_n [c] $\%10^{-3}$	Comp.[d] wt% PCHD
1	0.502	0.538	5.00	28.9	1.05	31.3	28.2	51.0
2	0.599	0.221	4.15	20.6	1.05	25.7	24.4	21.7
3	0.932	0.596	6.92	27.8	1.04	30.5	29.5	36.8
4	0.240	1.354	7.02	27.0	1.06	28.4	26.7	82.2
5	0.519	0.525	5.06	46.1	1.08	43.8		41.7
6	0.705	0.850	7.61	30.1	1.05	32.1	31.0	52.3
7	0.745	0.766	7.89	28.7	1.04	28.9	27.8	46.0
8	0.635	0.925	7.76	30.0	1.07	33.9	30.4	62.1
9	0.553	0.546	5.15	23.5	1.05	27.1	26.6	42.3

[a]: From SEC; [b]: from SEC-MALLS; [c]: from MALDI-TOF-MS; [d]: via ^{1}H-NMR in $CDCl_3$

Table 7 Characterization of 3-Armed PCHD Stars

Polymer	PCHD arm			3-Armed Star	
	$M_w{}^a$ ($\times 10^{-3}$)	$M_w/M_n{}^b$ ($\times 10^{-3}$)		$M_w{}^a$ ($\times 10^{-3}$)	$M_w/M_n{}^b$ ($\times 10^{-3}$)
KH5-033	7.3	1.04		21.4	1.06
KH5-041	5.8	1.07		18.3	1.05
KH5-051	13.6	1.05		41.2	1.06

[a]: From SEC-MALLS; [b]: From SEC

Table 8   Star-Block Copolymer Characteristics

Polymer	First block		Block Copolymer			Wt %	Star Block Copolymer		
	$M_n{}^a$ $(\times 10^{-3})$	$M_w/M_n{}^b$	$M_n{}^a$ $(\times 10^{-3})$	$M_w{}^c$ $(\times 10^{-3})$	$M_w/M_n{}^b$	PCHD^d	$M_w{}^c$ $(\times 10^{-3})$	$d_n/d_c{}^e$	$M_w/M_n{}^b$
Polystyrene as outer block									
KH5-057	9.8	1.02	14.8	15.7	1.03	26.8	46.2	0.160	1.04
KH5-062	2.3	1.08	15.5	15.7	1.08	80.4	47.3	0.136	1.04
KH5-067	5.6	1.04	13.9	15.3	1.06	54.0	43.9	0.148	1.05
Poly(1,3-Cyclohexadiene) as outer block									
KH5-071	4.7	1.10	14.2	15.3	1.06	31.2	45.1	0.158	1.05
KH5-077	13.4	1.07	16.6	18.1	1.08	74.1	49.4	0.139	1.06
KH5-081	14.2	1.08	24.9	27.1	1.09	56.3	74.9	0.147	1.07

^{a}: From MALDI-TOF-MS; ^{b}: via SEC; ^{c}: From SEC-MALLS; ^{d}: via ^{1}H-NMR; ^{e}: in ml/g and calculated from the weight composition and the dn/dc data for PS and PCHD in CHCl$_3$ (0.172 and 0.125 ml/g, respectively).

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Claims

1   1.   A nanostructured formation process comprising the steps of:

2   polymerizing a diene under conditions suitable to yield a structure

3 having at least one dimension ranging from 1 to 100 nanometers.

1

1   2.   The process of claim 1, wherein polymerization of the diene

2 occurs in the presence of a second monomer to form a block copolymer.

1

1   3.   The process of claim 1, wherein polymerization occurs under

2 conditions suitable for the structure to self assemble.

1

1   4.   The process of claim 1, wherein the diene comprises

2 cyclohexadiene.

1

1   5.   The process of claim 2, wherein the second monomer comprises

2 styrene.

1

1   6.   The process of claim 1, wherein polymerization occurs in the

2 presence of an additive.

1

1   7.   The process of claim 6, wherein the additive is selected from the

2 group consisting of TMEDA, DME, DABCO, and butyllithium.

1

1   8.   A nanostructure formed by the process of claim 1.

1

1   9.   The process of claim 1, wherein the structure is selected from

2 the group consisting of nanotube, star polymer, nanofiber, nanosphere and

3 brushes.

1

1   10.   A composite material incorporating the nanostructure formed by

2 the process of claim 1.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

(A)

(B)

FIGURE 9

FIGURE 10

FIGURE 11
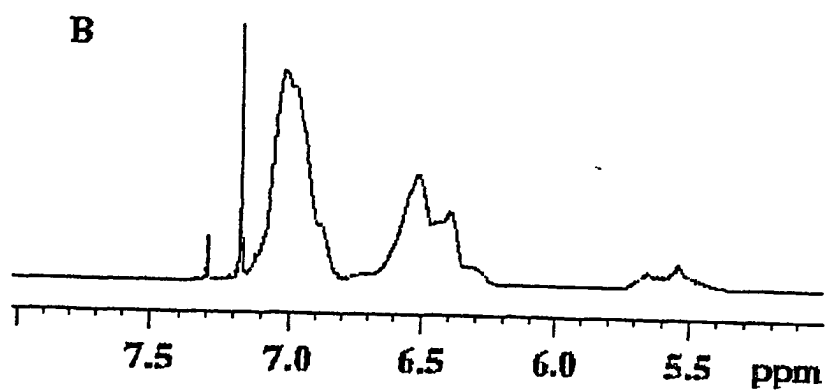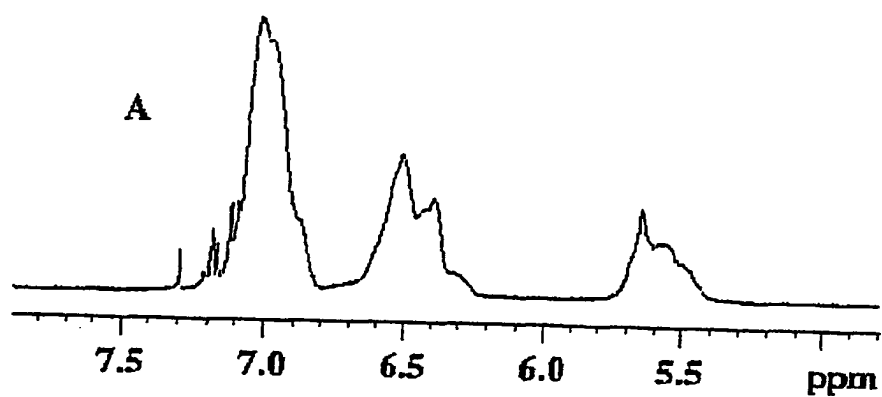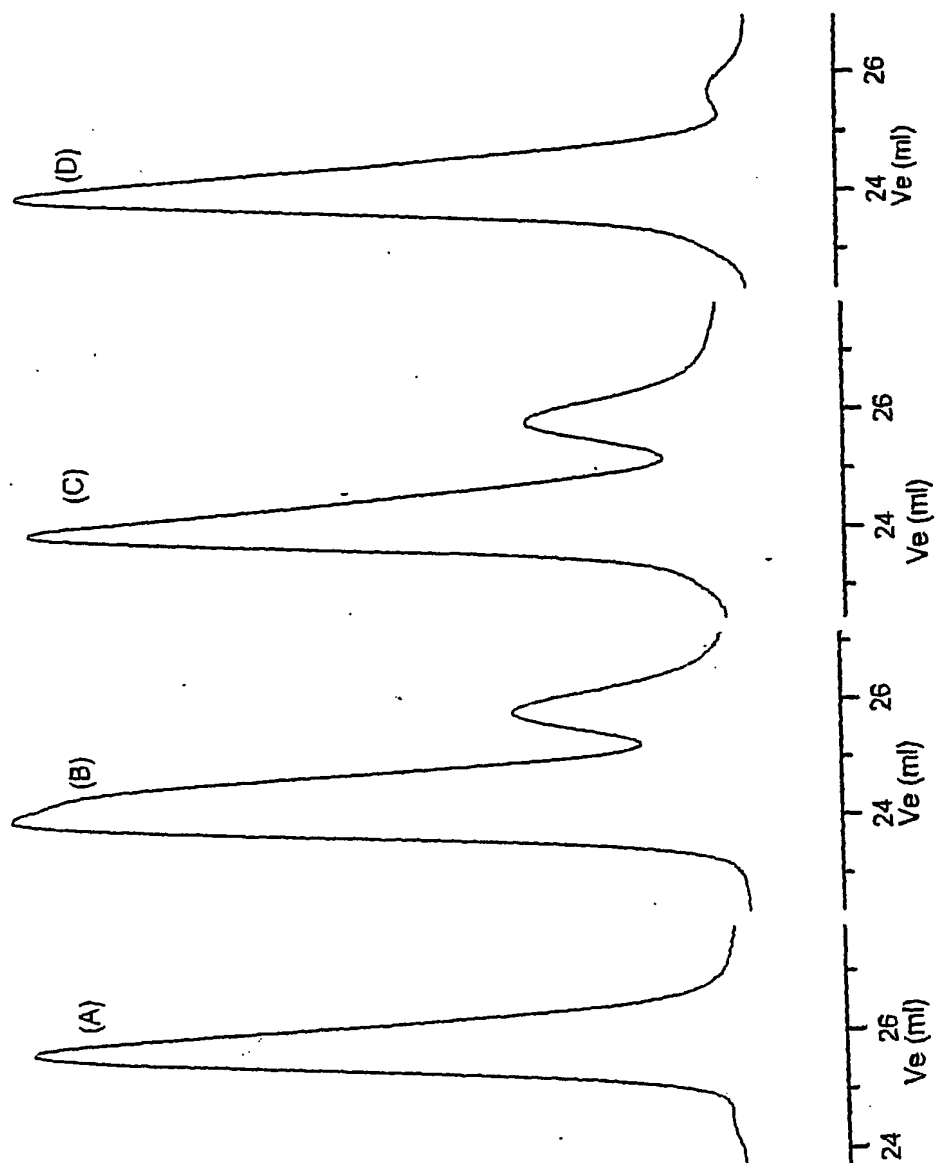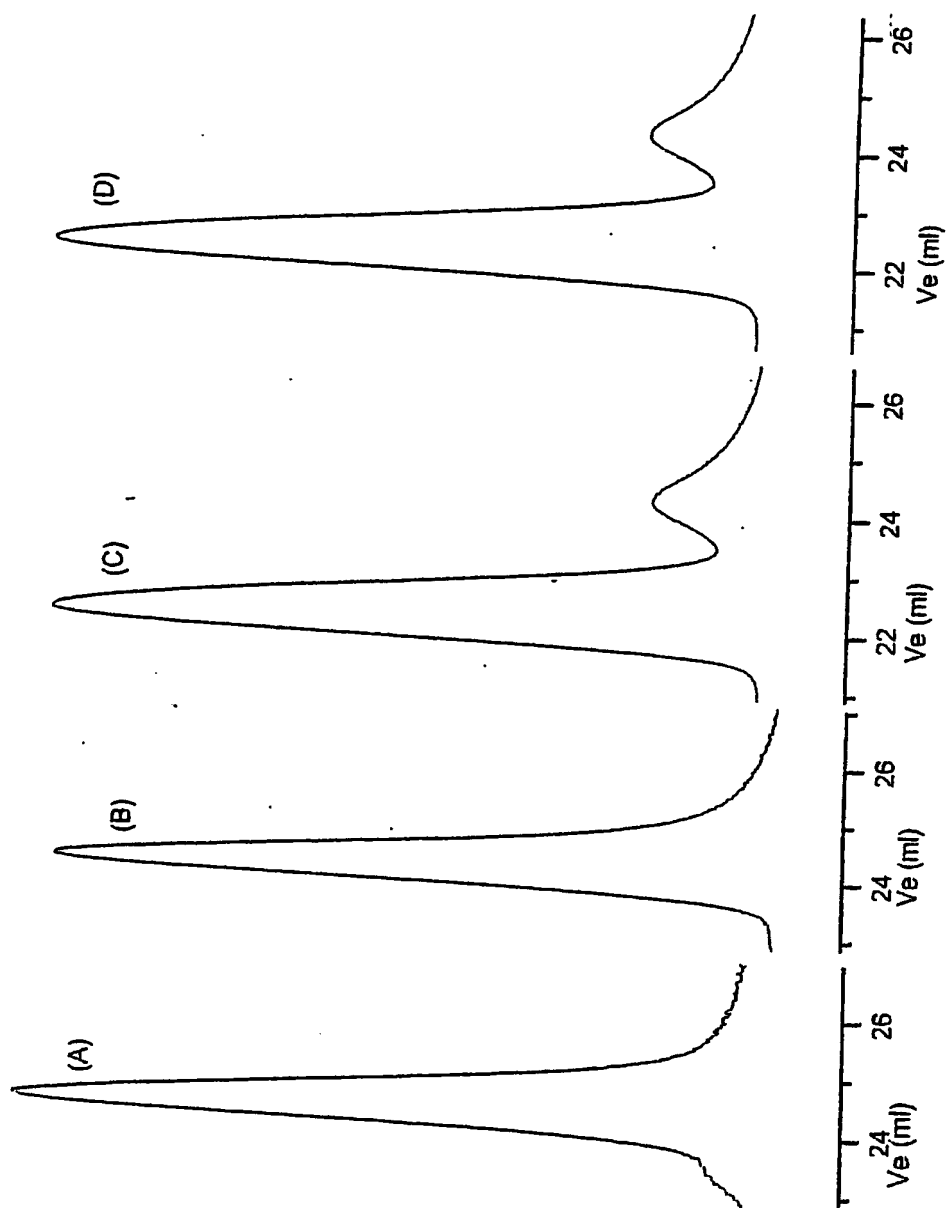
FIGURE 12
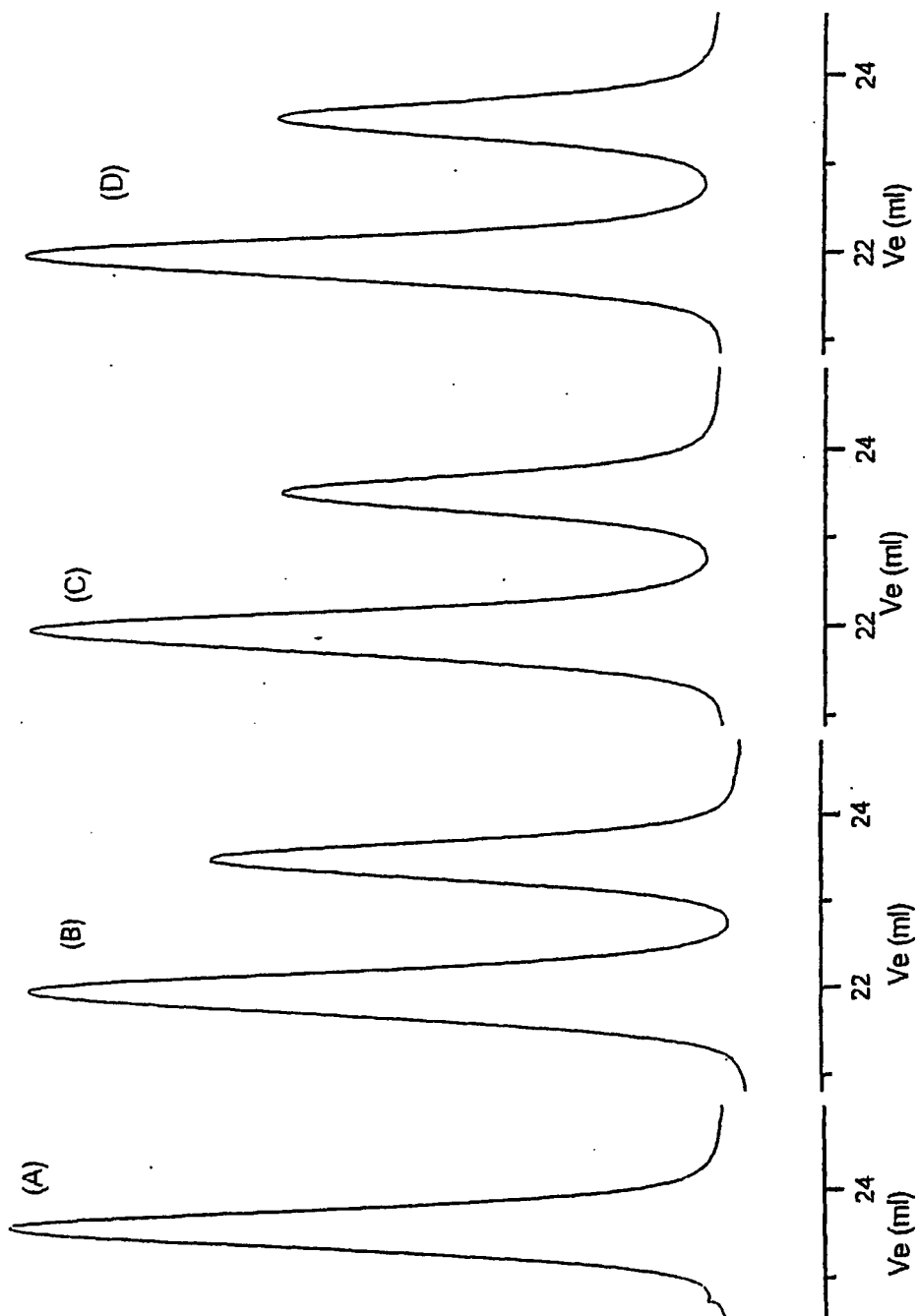
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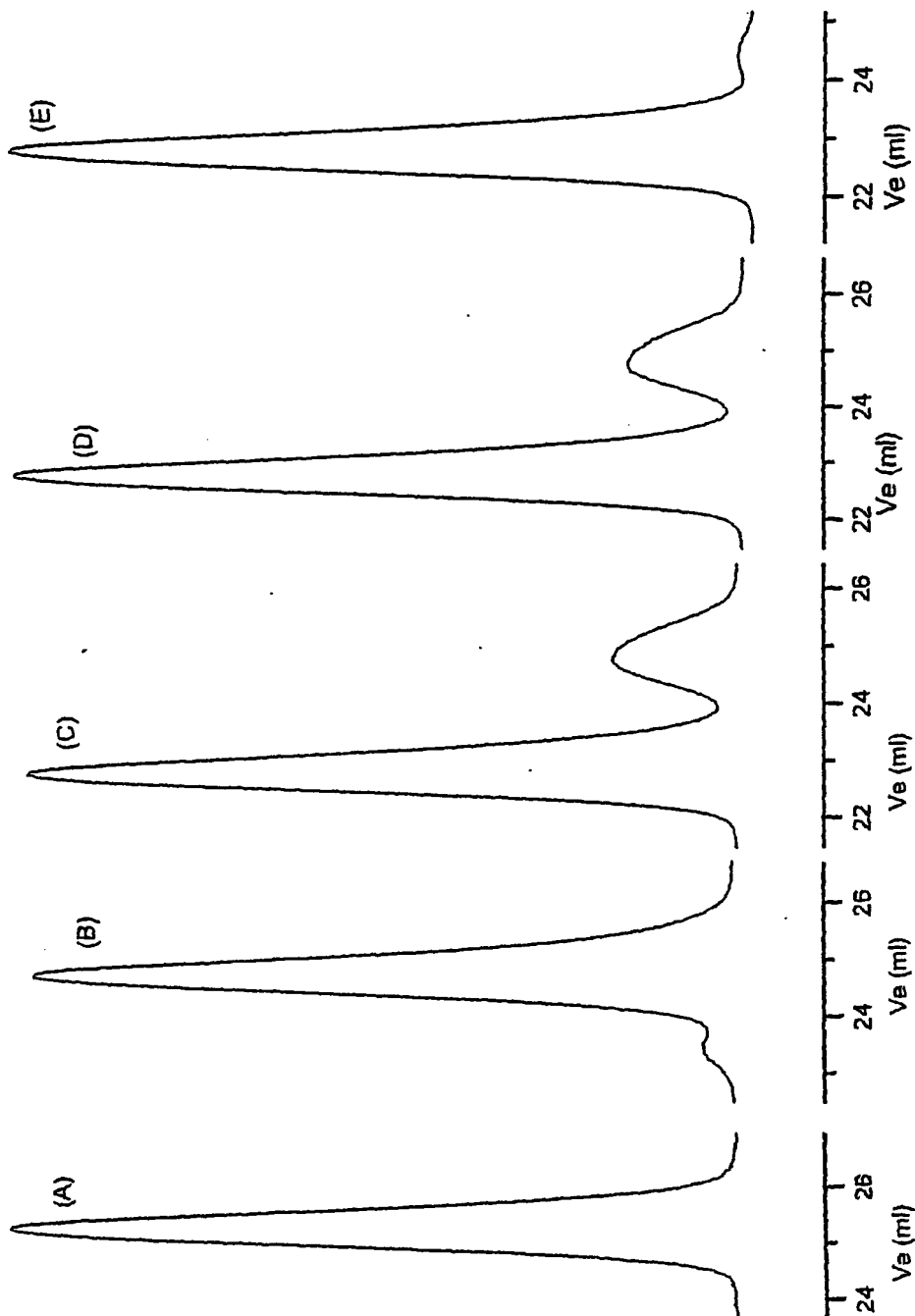
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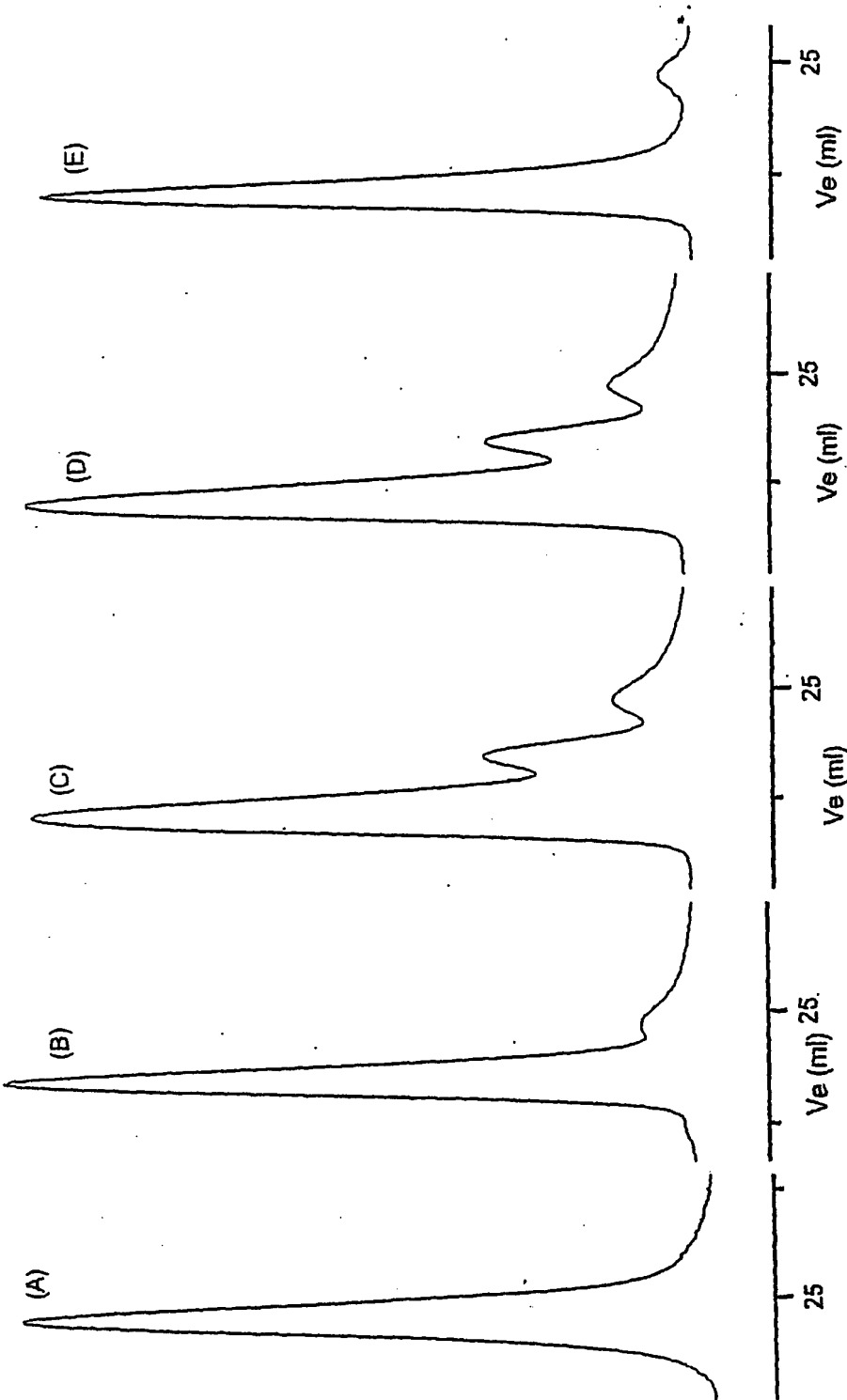
FIGURE 15

FIGURE 16

FIGURE 17

FIGURE 18b

FIGURE 18a
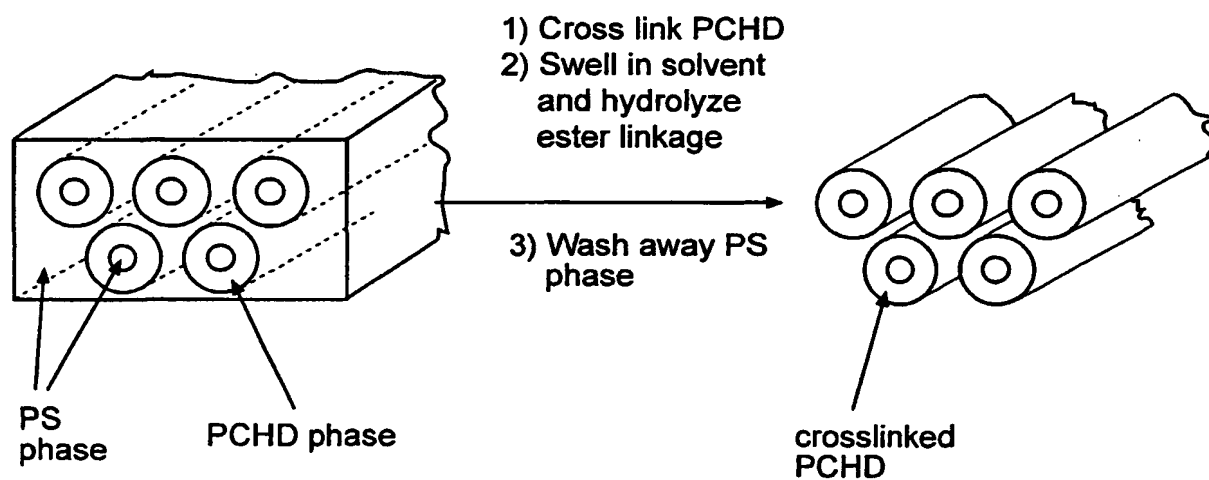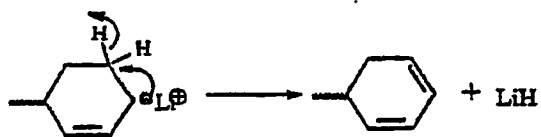
1) Cross link PCHD
2) Swell in solvent and hydrolyze ester linkage

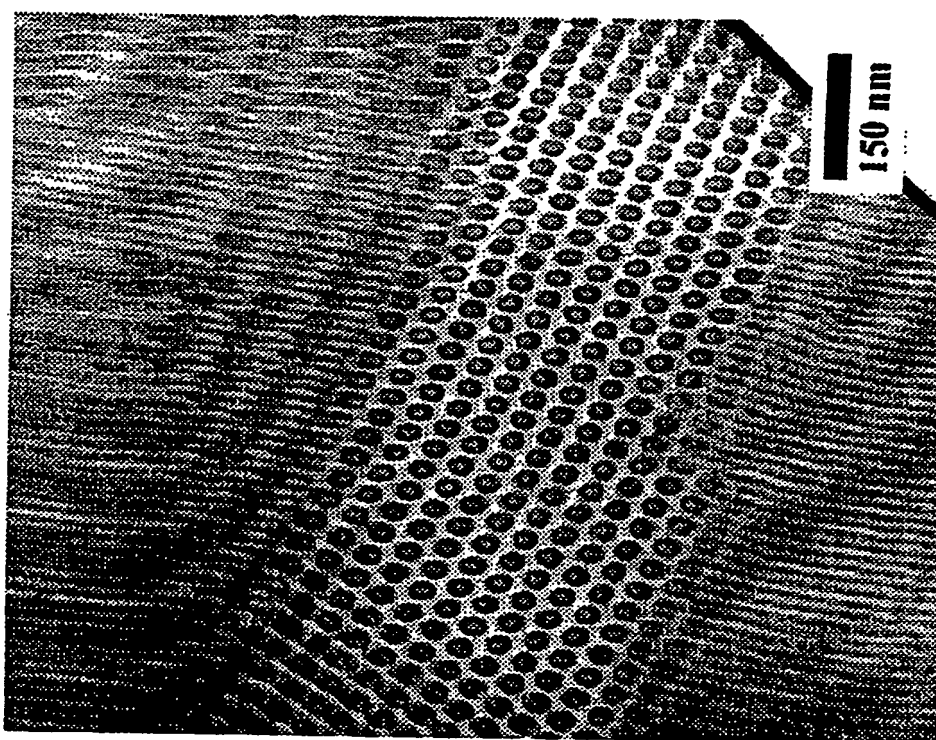3) Wash away PS phase

PS phase

PCHD phase

crosslinked PCHD

FIGURE 19

(a) Hydride elimination (chain termination)

(b) Proton abstraction (chain transfer to monomer)
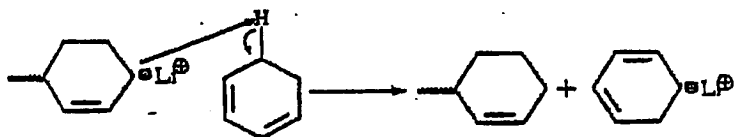
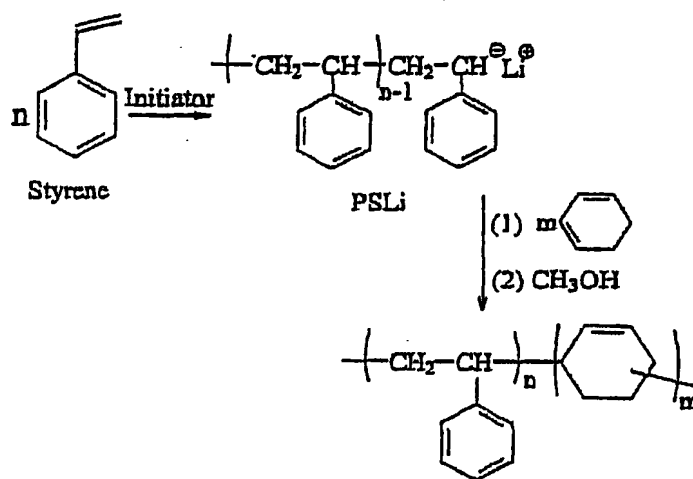(c) 1,4-addition and (d) 1,2-addition (chain propagations)
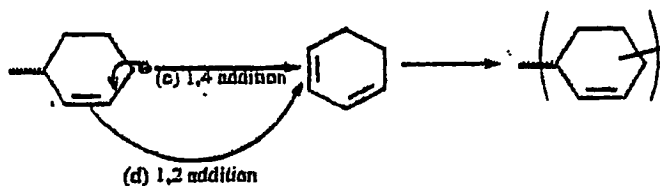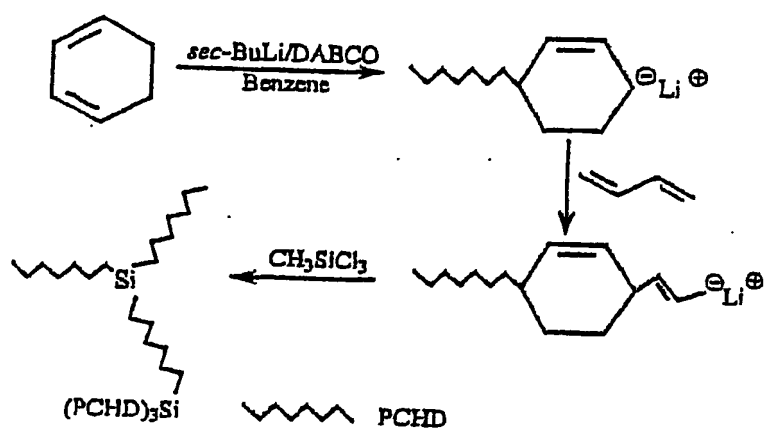

FIGURE 20

(A)
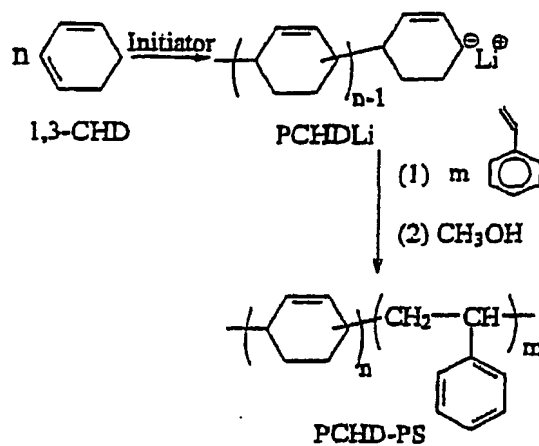
(B)

FIGURE 21

FIGURE 22
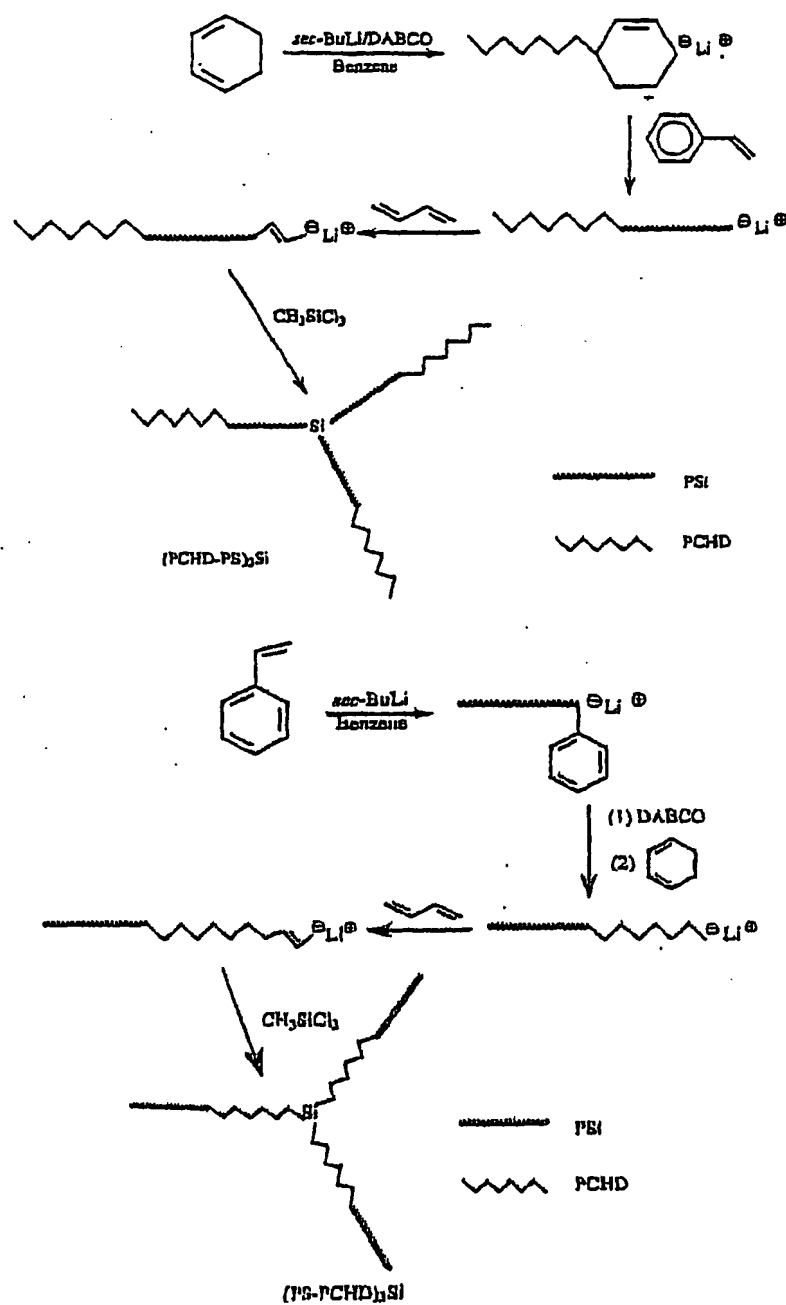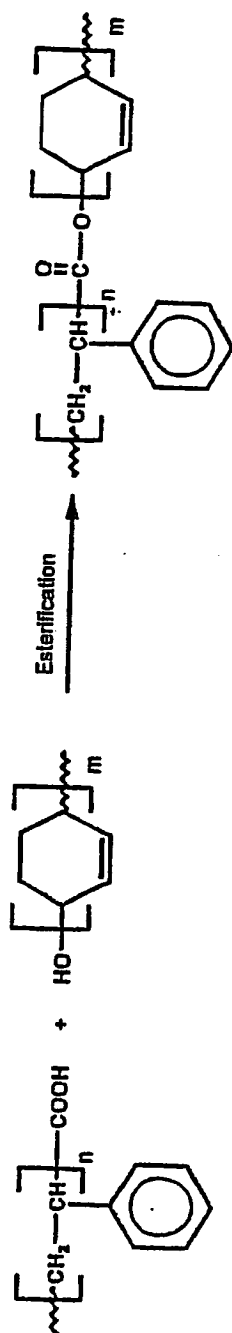
FIGURE 23

FIGURE 24

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C08F 32/06; C08L 53/02
US CL   :525/332.1, 328.5, 332.9, 333.1, 333.3; 526/308

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/332.1, 328.5, 332.9, 333.1, 333.3; 526/308

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST

search terms: diene, polymerization, nanometers, nanostructures

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,128,418 A (GRUBBS et al) 7 JULY 1992, col. 1, line 51, col. 10, lines 27 and 51	1, 3, 4
X	US 4,798,742 A (BALLARD et al) 17 JANUARY 1989, col.1, line 64, col. 2, line 55, col. 5, line 64	1, 3, 4, 6-8, 10

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 DECEMBER 2001	**03 JAN 2002**

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	OLGA ASINOVSKY
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